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Ollscoil na hÉireann, Corcaigh

**National University of Ireland, Cork**



# **Compositional and analytical factors affecting the stickiness of dairy powders**

Thesis presented by

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For the degree of Master of Research



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## Declaration

I hereby declare that I am the sole author of this thesis and it has not been submitted to any other University or higher education institute, or for any other academic award. Where reference has been made to the work of others, it has been fully acknowledged and referenced.

Signature:

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Laura O'Donoghue

04/10/2019

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**Abstract**

Spray drying is a dehydration technique used in the dairy industry for the preservation and creation of a wide range of valuable dairy products. However, challenges associated with stickiness development are often encountered during spray drying, particularly with spray dryer feed streams containing high levels of lactose, which can lead to lower yields, reduced powder quality and shorter runs. Stickiness in lactose-containing powders is related to the glass transition phenomenon, in which a phase change occurs in the amorphous form of lactose, causing a decrease in the viscosity of the powder particle surface, leading to liquid bridging and ultimately stickiness between particles and/or to equipment surfaces. There is a wide variety of compositional and environmental factors that affect the rate and extent of stickiness development in dairy powders, such as the temperature and relative humidity of the air or the protein content of the powder.

The first objective of this study was to investigate the influence of particle size on the physicochemical properties and stickiness behaviour of a selection of lactose-containing dairy powders. Using a fluidisation technique, this work demonstrated that stickiness increased with decreasing particle size for lactose-containing dairy powders.

Stickiness may be characterised using a number of different instrumental approaches, which can be categorised as direct/indirect or static/dynamic techniques. However, most methods provide a binary definition of stickiness (i.e., sticky or non-sticky), which while pragmatic, does not provide information regarding the mechanical relaxations which contribute to stickiness. Therefore, the second objective of this study was to examine the use of dynamic mechanical analysis (DMA) to characterise temperature- and humidity-induced relaxation behaviour of whey protein concentrate (WPC) powders; results were also compared to two other established techniques, differential scanning calorimetry (DSC) and a fluidisation method. The results demonstrated that while DMA may not be an accurate method for stickiness determination, it could prove useful as a complementary method when

combined with stickiness techniques (e.g., fluidisation) to provide more detailed information on the physical changes occurring during stickiness.

Overall, the findings of this research will prove useful to dairy processors at minimising issues with stickiness during drying and may also potentially provide powder technologists with a new method for tracking the physical transitions that occur during stickiness development of dairy powders.

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**Nomenclature**

(where applicable units included in parentheses)

$a_w$	water activity	
C16	fatty acid with 16 carbon chain (saturated)	
C18	fatty acid with 18 carbon chain (saturated)	
C18:1	fatty acid with 18 carbon chain and 1 double bond (unsaturated)	
C18:2	fatty acid with 18 carbon chain and 2 double bonds (unsaturated)	
Ca	Calcium	
$\text{Ca}_3(\text{PO}_4)_2$	Calcium Phosphate	
$\text{CH}_3\text{COOK}$	Potassium Acetate	
D[4,3]	volume mean diameter	( $\mu\text{m}$ )
$E'$	storage modulus	(M Pa)
$E''$	loss modulus	(M Pa)
$\text{K}_2\text{CO}_3$	Potassium carbonate	
LiCl	Lithium chloride	
$\text{MgCl}_2$	Magnesium chloride	
N	Nitrogen	
NaCl	Sodium chloride	
$\Delta T$	temperature difference	( $^{\circ}\text{C}$ )
T	temperature	( $^{\circ}\text{C}$ )
$T_a$	$\alpha$ -relaxation temperature determined using DMA	( $^{\circ}\text{C}$ )



$T_a$ onset	$\alpha$ -relaxation temperature of the onset in the decrease of the storage modulus	(°C)
$T_a$ peak	$\alpha$ -relaxation temperature of the peak of the loss modulus	(°C)
$T_f$	sticking temperature determined using the fluidisation method	(°C)
$T-T_g$	temperature difference between the glass transition temperature ( $T_g$ ) and sticking point temperature (T)	(°C)
$T_g$	glass transition temperature	(°C)
$T_{ge}$	glass transition temperature (endset)	(°C)
$T_{gi}$	glass transition temperature (onset)	(°C)
$T_{gm}$	glass transition temperature (midpoint)	(°C)

#### Greek Letters

$\alpha$	Alpha
$\beta$	Beta
$\delta$	Delta
$\kappa$	Kappa

**Abbreviations**

ANOVA	analysis of variance
BWL	bound water in the lactose
CC	casein content
DC	direct current
DSC	differential scanning calorimetry
DMA	dynamic mechanical analysis
DMTA	dynamic mechanical thermal analysis
DVS	dynamic vapour sorption
DWP	demineralised Whey Powder
ED	electrodialysis
FCMP	full cream milk powder
FFMP	fat-filled milk powder
FW	free water content
GAB	Guggenheim-Anderson-De Boer
GMP	glycomacropeptide
HCL	hydrochloric acid
IDF	International Dairy Federation
ISO	International Organisation for Standardisation
LA	lactic acid

LSD	least significant difference
MSSC	milk salt solution content
MPC	milk protein concentrate
N.D.	not determined
NDF	nano-diafiltration
NF	nanofiltration
NPN	non-protein nitrogen
PSD	particle size distribution
RH	relative humidity
RVP	relative vapour pressure
SD <sup>2</sup> P <sup>®</sup>	Spray Drying Parameters Simulation & Determination
SEM	scanning electron microscopy
SMP	skim milk powder
SPI	soy protein isolate
SPSS	Statistical Package for the Social Sciences
SPT	sticking point temperature
SSA	specific surface area
TCA	trichloroacetic acid
TW	total water content
UK	United Kingdom
USA	United States of America

WMP	whole milk powder
WPC	whey protein concentrate
WPC 20	whey protein concentrate (20% protein)
WPC 35	whey protein concentrate (35% protein)
WPC 50	whey protein concentrate (50% protein)
WPC 65	whey protein concentrate (65% protein)
WPC 80	whey protein concentrate (80% protein)
WPI	whey protein isolate
WPP	whey permeate powder
XPS	x-ray photoelectron spectroscopy

## **Chapter 1: Literature Review**

## 1.1 Introduction

The dairy industry is a key component of the Irish economy, with approximately 7 billion litres of milk processed annually (Food Drink Ireland, 2019). Spray drying is an essential dehydration technique that is widely used in the dairy industry for the production of a wide range of commodity and high-value dairy powders. One of the main challenges encountered by dairy processors, primarily during the spray drying stage of powder production, is that powders can become sticky. Although some advantages of stickiness exist, such as its exploitation in the agglomeration of powder, stickiness is generally considered to be a significant issue for the dairy industry. If powder sticks to drier walls it will eventually burn leading to reduced powder quality. In addition, excessive amounts of small powder particles or 'fines' in air filtration systems, such as cyclones and bag houses, will build up and block these systems, leading to lower product yields and longer processing times. All of these issues ultimately lead to economic losses and challenges with finished product quality for dairy producers. It is therefore essential that the product formulation and spray drying process be optimised in order to minimise issues with stickiness and maximise product yields.

The stickiness behaviour of a powder is strongly influenced by the composition of the concentrate, with feeds containing high proportions of carbohydrate being the most susceptible to sticking. Lactose is the primary carbohydrate found in milk and will be present in solution in one of two anomeric forms;  $\alpha$ - or  $\beta$ -lactose. However, when an aqueous lactose solution is concentrated very rapidly, such as during the spray drying process, the viscosity of the material increases so quickly that the mobility of the lactose molecules is reduced and they solidify without any ordered structure forming. Lactose that dries in this metastable, 'glassy' state is known as amorphous lactose, and this type of lactose is highly hygroscopic and thermodynamically unstable, which means it will readily change state when subjected to humid environments. This instability is the primary cause of problems during the processing and storage of powders with high lactose contents. However, other compositional

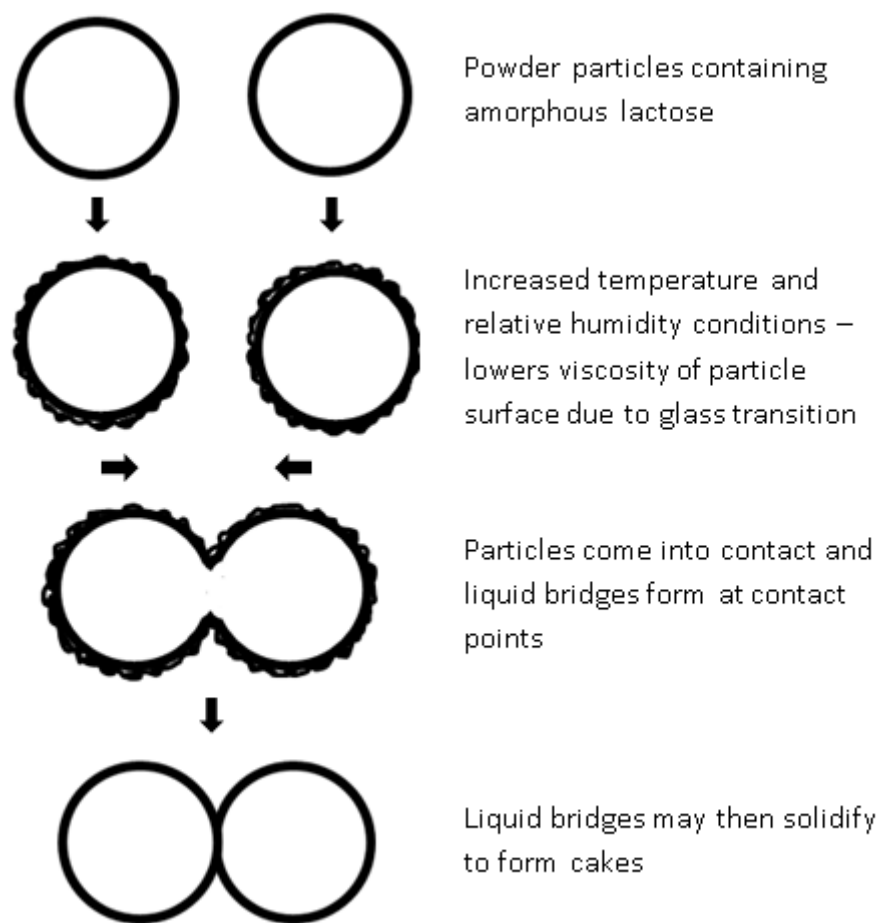
factors, such as the fat, protein or moisture content, can also play a significant role in the stickiness behaviour of dairy powders.

Several techniques have been applied industrially in an attempt to address challenges associated with stickiness. These include the use of dehumidified air, the addition of free-flowing agents, the modification of the drying chamber to include wall-sweepers, cooling of spray dryer walls and the alteration of processing parameters in order to ensure the powder is maintained at a temperature below its sticking point (Boonyai et al., 2004). Caking is another powder handling issue that is closely related to stickiness and manifests as the formation of hard lumps or 'cakes' during the storage of previously free-flowing powder. However, caking is not the focus of this thesis and therefore will only be briefly discussed in this review in the interests of clarity and completeness.

## **1.2 Mechanisms of stickiness**

### **1.2.1 Carbohydrate-based stickiness**

Stickiness is a surface phenomenon that occurs when powder particles come in contact with one another (cohesion) or equipment surfaces (adhesion) (Downton et al., 1982). Cohesion is an internal property and describes the forces that hold the particle together, whereas adhesion is an interfacial property that describes the forces that cause a particle to adhere to another surface (Boonyai et al., 2004). In order to prevent stickiness, forces greater than the cohesive and adhesive forces must be present. The extent of the cohesive or adhesive behaviour of the particle depends on the viscosity of the particle surface. If the viscosity is low enough, molecular mobility will increase and surface energy-driven viscous flow will occur. This allows liquid bridges to form between particles and/on equipment surfaces (Fig. 1.1). If these liquid bridges can resist subsequent mechanical deformations sticking will occur (Downton et al., 1982). Using sucrose/fructose mixtures, Downton et al. (1982) estimated that sticking occurs when the particle surface viscosity decreases



**Figure 1.1** Diagram showing the mechanisms of stickiness in dairy powder particles.

to between  $10^6 - 10^8$  Pa s. In dairy powders, lactose is the primary cause of this change in viscosity, due to a phase change it undergoes to a less viscous state. During spray-drying, the temperature and relative humidity (RH) of the outlet air are the primary factors that determine the particle viscosity due to their effects on the lactose. In order for sticking to occur, the particles also need to be in contact with one another for a sufficiently long time in order for liquid bridges to form and cohesion to occur.

#### 1.2.1.1 Relationship between glass transition and stickiness

The glass transition temperature ( $T_g$ ) of an amorphous system can be defined as the temperature at which a material-specific change in physical state occurs. Below the  $T_g$ , the material is kinetically frozen in a 'glassy' state and may be stored for extended

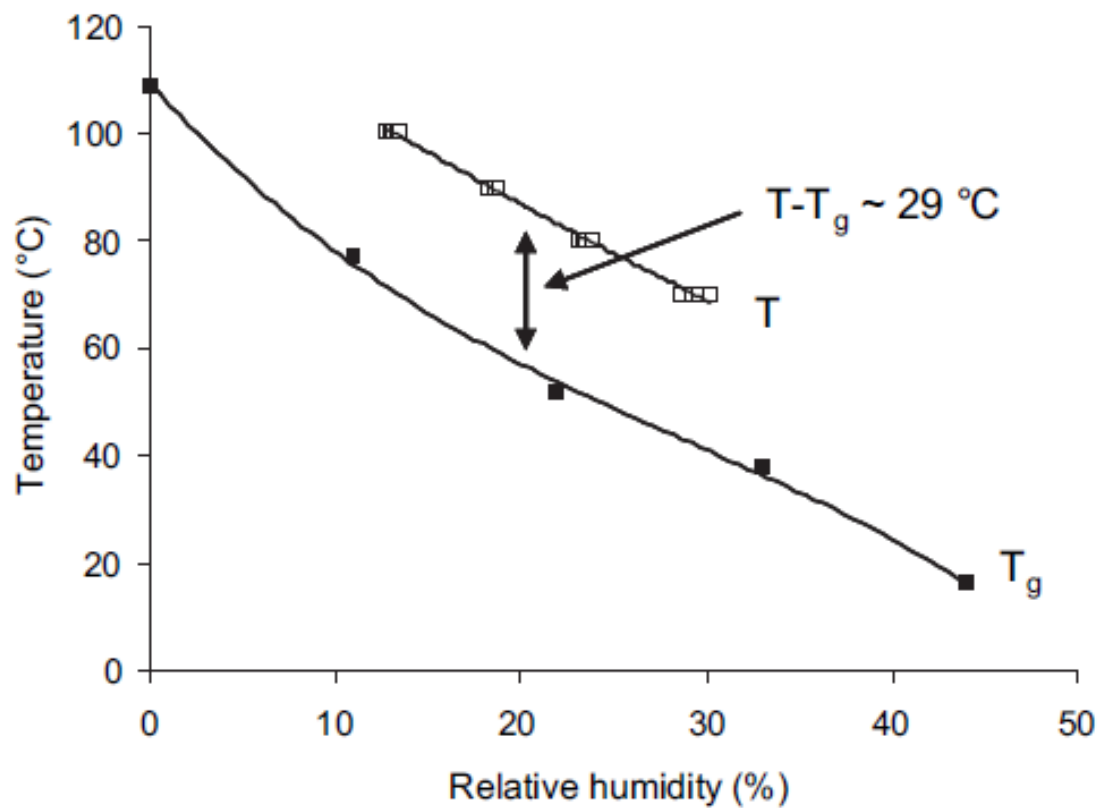


periods without difficulty. However, at and above the  $T_g$ , the molecular mobility of the material will increase and the amorphous glass will change from a solid to a more 'rubbery' state. The glass transition is generally observed over a temperature range but is most commonly reported as a single  $T_g$  value in the literature. For example, the  $T_g$  of anhydrous amorphous lactose has been reported as 101°C (Jouppila and Roos, 1994a). In lactose-containing dairy powders, the  $T_g$  is primarily determined by the amorphous lactose content of the powder (Shrestha et al., 2007; Silalai and Roos, 2010). Therefore, glass transition is closely related to stickiness, as the change in state of the amorphous lactose that occurs during the glass transition results in a reduction in the viscosity of the particle surface, leading to liquid bridging between particles and the onset of sticking. Furthermore, the susceptibility of a powder to sticking decreases as the  $T_g$  increases. However, it should be noted that glass transition is a bulk material property, whereas stickiness is a surface phenomenon, therefore some discrepancies can exist between glass transition and stickiness data.

#### 1.2.1.2 The use of $T-T_g$ in stickiness determination

The actual temperature at which sticking occurs, known as the sticking point temperature (T or SPT), usually occurs at temperatures greater than the  $T_g$  (Fig. 1.2). Many authors agree that the rate of stickiness development is related to the magnitude of the  $T-T_g$ , rather than the specific temperature and humidity conditions used to reach the sticking point (Foster et al., 2006; Murti et al., 2009; Paterson et al., 2005; Paterson et al., 2007). Roos and Karel (1991a) suggest that the sticking point temperature occurs approximately 10-15°C above the glass transition temperature. However, the extent to which the temperature must exceed the  $T_g$  before sticking occurs can vary significantly between powders as it is dependent on powder composition (Hogan et al., 2009). The measuring techniques used to determine both the  $T_g$  and SPT can also cause significant variation in the  $T-T_g$  values, even for the same powder. This is evident in the range of  $T-T_g$  values that have been reported for SMP; 29°C using a fluidised bed apparatus (Hogan et al., 2009; Hogan and O'Callaghan, 2010), 33.6°C using a particle gun (Murti et al., 2009), 14-22°C using a thermo-mechanical test (Ozmen and Langrish, 2002) and 23.3°C using a direct stirrer-

type technique (Hennigs et al., 2001). It is therefore not possible to provide exact  $T_g$  values for dairy powders due to the wide range of factors influencing both the measuring techniques and compositional variations between individual powders.



**Figure 1.2** Graph showing relationship between sticking point temperature ( $T$ ) and glass transition temperature ( $T_g$ ) for skim milk powder (SMP). Taken from Hogan and O'Callaghan (2010).

### 1.3 Overview of dairy products that are susceptible to sticking

#### 1.3.1 Products with high lactose contents

##### 1.3.1.1 Whey

Whey is liquid produced as a by-product of various coagulation processes in the dairy industry, such as cheese, acid casein or Greek-style yoghurt production. Historically, the nutritional value and potential of whey was not realised, and it was regarded as a waste product, often used as animal feed or fertilizer. In more recent years, there has been much development in the area of whey utilisation and valorisation, and it is now considered an important raw material for the production of many high-value products. Whey is composed of a complex mixture of water, lactose, minerals, proteins and fat, but the proportion of these components can vary significantly depending on the type of whey. The composition of a typical cheese whey is approximately 6% total solids, comprising of about 75–76% lactose and 13–14% whey protein (Písecký, 2005).

##### 1.3.1.1.1 Sweet whey

Sweet whey is produced as a by-product of cheese or rennet casein production. During the cheese production process rennet enzymes, such as chymosin, are used to cleave the  $\kappa$ -casein on the surface of the casein micelles, leading to the formation of a coagulum or 'curd' that will later become cheese. As this type of cheese is formed due to enzymatic precipitation, the pH of the resulting whey will remain close to the natural pH of milk, and is normally between pH 5.9 and 6.6. The process of cleaving the  $\kappa$ -casein releases *para*- $\kappa$ -casein and glycomacropeptide (GMP). The release of this GMP contributes to the higher protein content of sweet (1-0.9%) compared to acid whey (~0.7-0.5%) (Chandrapala et al., 2015; Durham, 2000; Nishanthi et al., 2017b). Salty whey is another type of cheese whey that is characterised by a high salt concentration that results from the addition of NaCl during the salting step of some hard cheese varieties, such as Cheddar. It should be noted that this high salt

concentration can cause issues during downstream processing, which will be discussed later in the review.

#### 1.3.1.1.2 Acid whey

Acid whey is produced as a by-product of selected acidification processes, such as acid casein, cottage cheese or Greek-style yoghurt production. The production of acid casein involves the addition of acid (normally HCL) to decrease the pH of milk to the isoelectric point of the casein (~ pH 4.6), neutralising the negatively-charged casein micelles and causing them to precipitate out of solution. The whey produced from this process will therefore have a much lower pH, between 4.3 – 4.6, compared to sweet whey (Bylund, 1995). Acid whey also has a higher calcium (Ca) content compared to sweet whey as Ca is more soluble at lower pH and will therefore migrate with the whey protein in solution, rather than the casein fraction. Processing of acid whey is considerably more challenging than sweet whey due to its high lactic acid (LA) and mineral content (Nishanthi et al., 2017a), which cause fouling of membranes and stickiness to occur during spray drying (Bylund, 1995; Chandrapala and Vasiljevic, 2017). The challenges associated with processing of acid whey are discussed in further detail later in the review (see Section 1.5.1.2).

Greek-style yoghurt production also includes an acidification step, but it is bacteria that are responsible for the lowering of the pH. To produce Greek-style yoghurt the milk is first subjected to a high heat treatment step (90°C for 5 min) (Bong and Moraru, 2014), designed to denature the whey proteins, exposing the active thiol groups and allowing them to engage in thiol–disulphide exchange reactions with caseins. These aggregated whey proteins will later become incorporated into the casein-based coagulum, lowering the overall protein content of the whey compared to whey from acid casein production. This lower protein content will have implications on the stickiness behaviour of the powder produced from this whey. The milk is then inoculated with starter culture bacteria (normally *Streptococcus thermophiles* and *Lactobacillus bulgaricus*) and fermented for a given period of time (~6 h), or until the desired pH is reached. As the bacteria grow, they will convert the

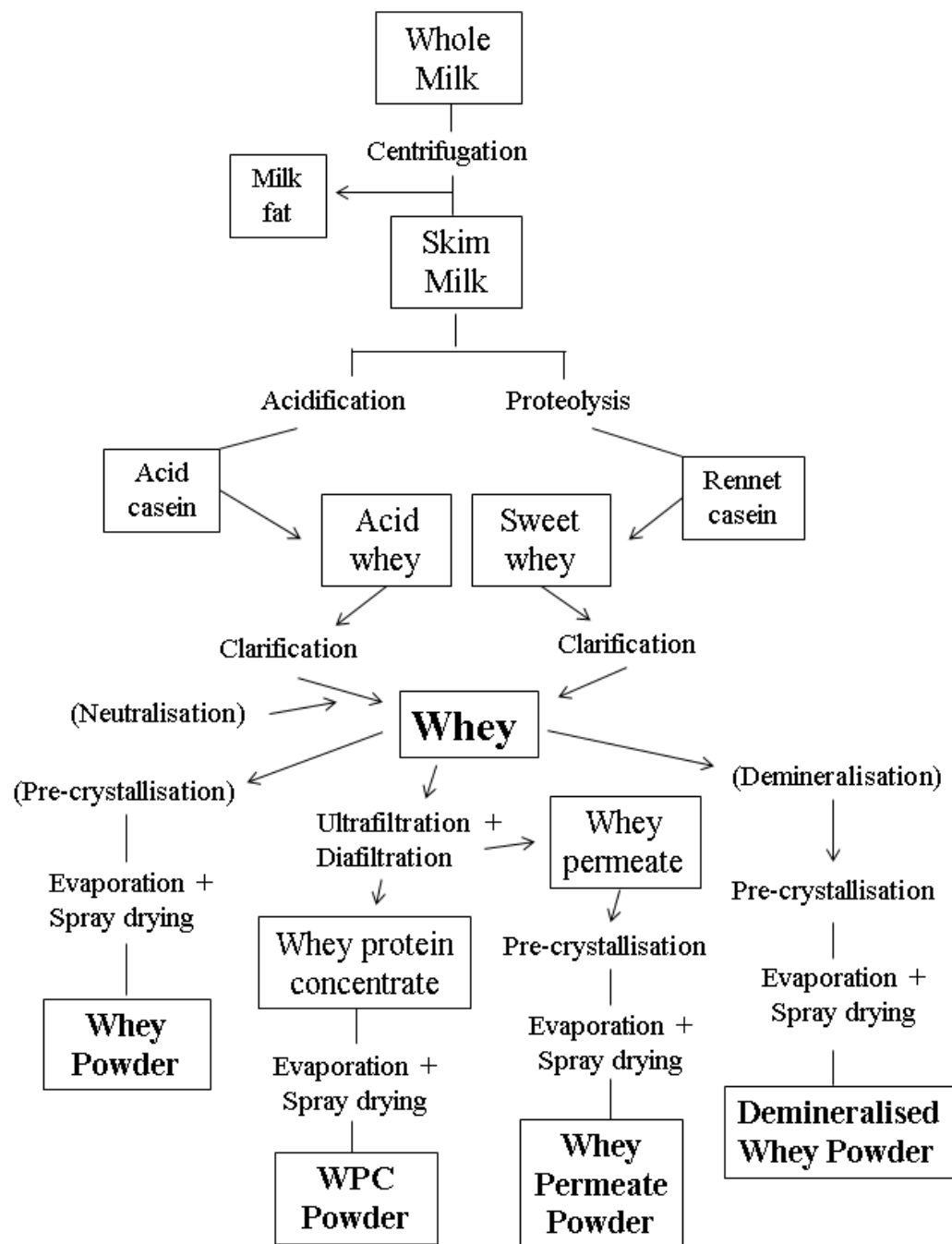
lactose present into LA, gradually lowering the pH and causing the casein to precipitate out of solution. Traditionally, the curds are then separated and strained through a cloth bag until the desired solid content is reached. In larger scale production centrifugal separators or membranes are used to separate the curds and whey.

#### 1.3.1.1.3 Native whey

Native whey (also referred to as virgin or ideal whey) is produced using a combination of various membrane processes (microfiltration, diafiltration and ultrafiltration) at low temperatures ( $\sim 45\text{-}50^{\circ}\text{C}$ ) to concentrate the protein fraction of the defatted whey stream. As an evaporation step is not required, the proteins are not subjected to high temperatures and remain in their native state. These native proteins possess enhanced functional properties compared to partially denatured whey proteins, such as improved solubility, gelation and foaming properties (Heino et al., 2007).

#### 1.3.2 Whey processing

Whey can be processed in a large number of different ways to produce a variety of quality products. These include whey powders, whey protein concentrate (WPC) powders, whey permeate powders and demineralised whey powders (Fig. 1.3). Due to its composition, whey must be processed as soon as possible after collection in order to prevent the growth of bacteria. It is recommended to cool the whey to less than  $10^{\circ}\text{C}$  if it is not being processed immediately (Písecký, 2012). If the whey is being stored for more than 15 h a pasteurisation step will be required. Regardless of the end product, the remaining fat and casein fines in the whey must first be separated out in order to increase the economic yield and also prevent problems during subsequent processing (Písecký, 2005). The casein fines are normally removed using a centrifugal clarifier and are often treated in the same way as cheese, and can be pressed and ripened to be used in cooking. Centrifugal separators are used to remove the remaining fat from the whey, and this whey cream by-product is often used in cheese-making to standardise cheese milk (Bylund, 1995).



**Figure 1.3** Flow diagram of whey processing.

#### 1.3.2.1 Whey Protein concentrates

The production of whey protein concentrate (WPC) is one of the most common ways to process whey due to its high product value and wide applications for use. These applications include the production of baby food, bakery products or sports nutrition products. WPCs are produced using a combination of ultrafiltration and diafiltration,

in order to concentrate the protein fraction to between 35 and 85% of the dry matter. The most common WPCs on the market are those that contain 35, 60 and 80% protein, with WPC 80 being the most common and most valuable (Písecký, 2012). The whey is usually first concentrated using ultrafiltration to a solids content of 25%; this is considered the upper limit for economic operation. The concentrate will then undergo diafiltration, which involves adding water to the feed/retentate in order to wash out low molecular weight components, until the desired protein content is achieved. Due to their higher protein content, WPC don't tend to cause many issues with stickiness during spray drying. However, the powders do tend to be very light and fluffy with high contents of occluded air (i.e., low bulk density).

#### 1.3.2.2 Whey permeates

Whey permeate is produced as a by-product of WPC production. Similarly to WPC, whey permeate is normally spray dried to produce whey permeate powder, which is often used as a bulking agent in products such as instant soups, sauces and confectionary (Písecký, 2005). The main constituent of these powders is lactose (~85%), which is present in a predominantly crystalline state, due to the pre-crystallisation step that the concentrate undergoes after evaporation and before spray drying. The main aim of this step is to convert the amorphous lactose present into the crystalline state in order to create a less hygroscopic and more stable powder. The importance of this pre-crystallisation step and the type of crystals produced will be discussed in more detail later in the review (see Section 1.5.1.1). After crystallisation, the solution is spray-dried using an atomiser wheel, and the final moisture is normally removed from the powder in a vibrating fluid bed.

#### 1.3.2.3 Demineralised whey permeates

Due to its high mineral content (8-12% dry weight), the applications of whey can be limited. For this reason, whey is often put through a demineralisation (or desalination) step in order to partially (25-30%) or almost fully (90-95%) remove the salts present. The partial demineralisation of whey is carried out using a process known as nanofiltration (NF), which uses 'leaky' RO membranes that allow through

small particle species with radii in the nanometer ( $10^{-9}$  m) range. These include certain monovalent ions, such as sodium and potassium, and small organic molecules such as urea. Partially demineralised concentrates are used in the production of ice-cream and bakery products.

High degree demineralisation (90-95%) is normally achieved using electrodialysis (ED). This is a membrane process during which ions are transported through non-selective, semi-permeable membranes under the influence of a direct current (DC) in an electrodialysis cell. The membranes used are either cation- or anion-selective, which means they will either allow positive or negative ions to flow through. ED can be done in batch or continuous conditions and the extent of demineralisation is determined by factors such as ash content of the whey, residence time and viscosity. Due to the high cost of replacing membranes, it is often more economical to use an ion exchange process to achieve demineralisation levels of  $\geq 70\%$ . Ion exchange involves the use of resin beads, which are normally in fixed columns, to adsorb mineral ions from solution and replace them with either  $H^+$  or  $OH^-$  ions. Their capacity for this is finite, so the adsorbed minerals must be removed and regenerated, normally using weak acid/bases, before re-use. One of the primary uses of highly demineralised whey powder (90-95%) is in the production of infant formula.

### 1.3.3 High-fat products

#### 1.3.3.1 Full cream milk powder

Full cream milk powder (FCMP), also known as whole milk powder (WMP), is produced by spray drying standardised, homogenized and pasteurised whole milk. FCMP generally has a fat content of between 26-28% (Kim et al., 2002). However, the fat content at the surface of the particle will be much higher, approximately 60-63% (Nijdam and Langrish, 2006), which can cause issues with stickiness during spray drying and subsequent storage. Soy lethicin is also commonly added to the powder during spray drying to produce instant full cream milk powder with improved functional properties, such as powder rehydration (Sanderson, 1978). The main



applications of FCMP are in the manufacture of chocolate, ice cream and other baked goods.

#### **1.4 Factors affecting stickiness**

As previously mentioned, lactose is the predominant cause of stickiness in dairy powders (Özkan et al., 2002; Silalai and Roos, 2010), primarily due to the influence of the glass transition on the viscosity of the particle surface. Therefore, increasing the amount of amorphous lactose in semi-crystalline dairy powders will increase the powders susceptibility to sticking (Hogan et al., 2009; Hogan and O'Callaghan, 2010). However, there are a wide variety of other compositional and environmental factors that will significantly influence the stickiness behaviour of dairy powders. Adhikari et al. (2001) reviewed many of these factors and assigned them a value based on their relative contribution to stickiness (Table 1.1). It should be noted that this review was written nearly 20 years ago and since then many new studies have emerged furthering our understanding on the influence of certain factors on the stickiness behaviour of powders. For example, in the review by Adhikari et al. (2001) the authors assigned protein a 'negligible contribution' to stickiness, yet in a study by Hogan and O'Callaghan (2010), the authors showed that protein can significantly affect the stickiness behaviour of a dairy powder. For this reason, an updated review of the factors influencing the stickiness of dairy powders and their effect on the glass transition is required.

**Table 1.1** Factors affecting stickiness of dairy powders and their relative contribution to stickiness. Taken from Adhikari et al. (2001).

Factors	Relative Contribution to Stickiness
Protein	o
Polysaccharides	o
Fats	+
Low molecular sugars	++
Organic acids	++
Water/relative humidity	+++
Particle size distribution	+
Compression/pressure	++
Temperature	+++
Viscosity	+++

o, base point (negligible contribution); +, high contribution; ++, higher contribution; +++, highest contribution.

#### 1.4.1 Effect of protein

Proteins are large molecules with high molecular weight and would therefore be expected to increase the  $T_g$  of dairy powders (Roos and Karel, 1991c). However, studies on the direct effect of protein on the  $T_g$  of dairy powders have reported mixed results. Maidannyk and Roos (2017) examined the  $T_g$  of protein/lactose powders at different protein:lactose ratios and water activities and found that in anhydrous conditions the  $T_g$  increased with increasing proportion of protein. Similarly, Haque and Roos (2004a) reported that the addition of various proteins (Whey Protein Isolate (WPI), albumin and gelatin) in 1:3 ratios to lactose, increased the  $T_g$  only slightly in the anhydrous state. However, mixed results were observed on  $T_g$  when these samples were humidified (up to  $a_w$  of 0.44). In the study by Maidannyk and Roos (2017), the  $T_g$  decreased slightly with increasing protein content, whereas in the study by Haque and Roos (2004a) the  $T_g$  increased in the presence of protein at  $a_w > 0.33$ . Using theoretical  $T_g$  curves, derived from the Couchmann-Karas equation, Hogan and O'Callaghan (2010) found that altering the protein content of a dairy powder only resulted in minor changes in the  $T_g$ . In contrast, Shrestha et al. (2007)

reported that adjusting the amount of protein in SMP/lactose mixtures did not affect the  $T_g$  of the different powders at equivalent water activities. In a subsequent study by Shrestha et al. (2008), the authors reported that increasing whey permeate addition (and therefore decreasing the protein fraction) of SMP decreased the  $T_g$  of the powder. Overall, these results suggest that proteins can increase the  $T_g$  in anhydrous conditions, but in multi-component systems where moisture is present, the influence of moisture sorption by amorphous lactose on the  $T_g$  may be more significant than that of protein.

Although results on the direct influence of protein on the  $T_g$  of dairy powders are inconsistent, studies have shown that the addition of protein to dairy powders can have a protective effect against sticking, due to the impact on the  $T-T_g$  (Hogan and O'Callaghan, 2010; Shrestha et al., 2008). Hogan and O'Callaghan (2010) superimposed stickiness curves on to  $T_g$  curves and found that the  $T-T_g$  increased as the proportion of protein in the powder increased. The authors suggested that the effects of proteins during stickiness development could be similar to those that occur during time-dependent lactose crystallisation, where the presence of protein has been shown to delay crystallisation due to protein-carbohydrate interactions. They hypothesise that competitive/preferential sorption of water by the proteins delays the uptake of water by amorphous lactose, hence delaying the physical change of the lactose from a 'glassy' to a more 'rubbery' state. The rate of stickiness development has also been shown to occur less rapidly in powders with higher protein contents (Silalai and Roos, 2010).

#### 1.4.2 Fat-induced stickiness

Unlike carbohydrate-based stickiness, which occurs due to a phase change and a subsequent change in viscosity, fat-induced stickiness is a result of melting behaviour. Milk fat has a low melting point and liquefies at temperatures greater than room temperature, leading to the formation of relatively weak junctions/bridges between powder particles. If the powder is cooled, these bridges can crystallise and solidify to form much stronger bonds between particles (Rennie

et al., 1999). This is particularly problematic during powder storage, as it can lead to issues with caking (Foster et al., 2005a). Alternatively, liquefaction of fat can also cause softening of the powder particle, leading to deformation of the particle structure and a subsequent increase in the contact area between particles (Rennie et al., 1999).

In a study by Rennie et al. (1999), the authors compared the cohesion of dry whole milk powder (WMP) and SMP and showed that the cohesion of WMP was nearly twice that of SMP at the same temperature. Özkan et al. (2002) also examined the differences in stickiness between SMP and WMP and showed that below the SPT, the cohesion (measured as torque) of the WMP was higher than that of the SMP. However, after the SPT, the SMP cohesion was much higher due to the influence of the glass transition on the lactose present. This study shows that although both fat and lactose can cause bridges/junctions to form between powder particles, these bridges are not equal in strength, and those formed by lactose are considerably stronger than those formed by fat.

#### 1.4.2.1 Fat content at the surface

Studies have shown that fat is not distributed homogeneously throughout dairy powder particles as it tends to be over-represented at the surface (Foerster et al., 2016; Kim et al., 2002; Nijdam and Langrish, 2006; Shrestha et al., 2007). This will have repercussions on the stickiness behaviour of a powder as stickiness is a surface phenomenon and will therefore be most affected by the surface (free) fat content. This is especially true for powders such as WMP, which can have surface fat contents of approximately 98% (Kim et al., 2005a). The proportion of fat at the surface of a powder is affected by factors such as the fat content of the bulk (Nijdam and Langrish, 2006), processing conditions (Kim et al., 2009), degree of saturation of the fat (O'Neill et al., 2019) and type of fat (O'Neill et al., 2019). In an early study by Buma (1971), the authors found no correlation between free fat content and cohesion for powders of similar particle size. However, later studies by Fitzpatrick et al. (2007) showed that surface fat had a major influence on powder cohesion, with higher surface fat

contents leading to greater cohesiveness. Although a similar trend was reported by Foster et al. (2005a), the authors claimed that the increased cohesion is only observed when the fat bridges partly solidify due to a decrease in temperature.

#### 1.4.2.2 Relationship between fat and protein content

Many fat-containing dairy powders, including WMP and fat-filled milk powder (FFMP), also contain proteins, which act as emulsifiers to encapsulate fat within the powder particles. During homogenisation, the proteins will adsorb to the newly formed oil-water interface, protecting the oil droplets against coalescence and providing stability to the emulsion during subsequent processing (Vega and Roos, 2006). Fat can therefore exist in two main forms in powder particles: as free/non-encapsulated fat, which consists of surface and inner fat, or encapsulated fat, which is located in the bulk of the powder. Proteins therefore play an essential role in preventing the creation of non-emulsified fat, which will manifest itself as free fat in the dried powder (O'Neill et al., 2019; Vignolles et al., 2007). In a study by Twomey et al. (2000), the authors found a linear relationship between the protein content of the milk and the free-fat content of the resultant spray dried powder. Fat is therefore thought to only cause significant issues with fouling and handling when fat contents are excessive enough that the encapsulation by proteins is inhibited (Kim et al., 2005b). O'Neill et al. (2019) investigated the effects of varying protein content on spray-dried dairy emulsions, with the aim to find the optimal protein content that would produce a powder with the lowest possible free fat content, thus protecting against sticking. They reported that emulsions with between 2-5% w/w protein all produced powders with free fat contents below the typical levels found in industrially produced powders (4 g per 100 g) (O'Neill et al., 2019).

#### 1.4.3 Moisture content

It is necessary to tightly control the moisture content of a dairy powder and its surrounding environment due to the effects of water on the glass transition phenomenon. It is well known that water acts as a plasticiser in an amorphous system by increasing the molecular mobility, causing the phase transition to occur at a lower

temperature. Many studies have shown that an increase in moisture leads to a decrease in the  $T_g$  of dairy powders (Haque and Roos, 2004b; Jouppila and Roos, 1994a; Maidannyk and Roos, 2017; Roos and Karel, 1991c; Silalai and Roos, 2010; Shrestha et al., 2007; Shrestha et al., 2008,). Stickiness behaviour is therefore significantly affected by moisture content, as increasing  $a_w$ /moisture content will decrease the  $T_g$ , resulting in a decrease in the SPT (Downton et al., 1982; Özkan et al., 2002; Silalai and Roos, 2010) and an increase in the rate of stickiness development (Murti et al., 2009). However, it should be noted that during spray drying, the  $T_g$  of the powder will actually increase as moisture is removed from the particles. Moisture uptake during storage is equally problematic, as this will cause the powder to adhere together in a process known as caking. The mechanisms of caking and the significance of moisture sorption on this process will be discussed in more detail later in this review (see Section 1.5.2.1).

#### 1.4.4 Particle size

The size of powder particles depends on many factors, such as the conditions used during processing, type of atomisation and composition of the feed solution. Particle size is thought to play a role in stickiness behaviour as cohesive and adhesive forces are inversely related to particle size, with smaller particles demonstrating more cohesive behaviour and *vice versa* (Buma, 1971; Geldart et al., 1984; Modugno et al., 2015; Rennie et al., 1999). Particle size may also influence stickiness due to the increased specific surface area (SSA) created by smaller particles. The increased contact areas between particles allows for the formation of more liquid bridges and, hence, an increase in stickiness. To date, very little research has been conducted on the relationship between particle size and stickiness in dairy powders. Hogan et al. (2009) compared the stickiness behaviour two SMP powder samples with volume mean diameter ( $D[3,4]$ ) values of 61 and 130  $\mu\text{m}$  using a fluidised bed apparatus, but found no significant difference in stickiness behaviour between the two samples. Although research on the relationship between stickiness and particle size may be limited, many studies (Carpin et al., 2017a; Modugno et al., 2015) have examined the

effect of particle size on caking in dairy powders and have shown that smaller particles have a higher tendency to cake, compared to larger particles.

#### 1.4.5 Molecular weight of carbohydrate component

The  $T_g$  of amorphous carbohydrates can also be influenced by their molecular weight (Roos and Karel, 1991c). Therefore, the stickiness behaviour of a dairy powder may be influenced by the molecular weight of the amorphous carbohydrates present due to the relationship between stickiness and  $T_g$ . For example, Jouppila and Roos (1994a) showed that hydrolysing lactose into glucose and galactose in SMP significantly decreased the  $T_g$  of the powder, compared to the original. Conversely, some studies (O'Neill et al., 2019; Roos and Karel, 1991c; Silalai and Roos, 2011b) have also investigated the addition/substitution of certain high-molecular weight polymers, such as maltodextrins, to feeds before drying in an attempt to increase the overall  $T_g$  of the resulting powder. Furthermore, it should be noted that although these studies have shown that increasing the molecular weight of the carbohydrate component in dairy powders can successfully increase the overall  $T_g$  of the powder, no studies have yet to examine whether this would have a direct effect on the stickiness behaviour of these powders.

### 1.5 Stickiness during processing and storage

#### 1.5.1. Processing

##### 1.5.1.1 Lactose pre-crystallisation

During spray drying, water is removed too rapidly for crystallisation of the amorphous lactose to occur and the amorphous lactose present will dry in a 'glassy' state. In many dairy powders, it is the instability of this amorphous lactose that leads to problems with subsequent handling and storage, such as issues with stickiness and caking. For this reason, feeds containing high amounts of amorphous lactose are often subjected to a pre-crystallisation processing step before drying. Lactose crystallisation involves a series of complex reactions but can generally be divided into

three main steps; nucleation, growth and mutarotation. These steps are strongly influenced by the processing conditions used, such as the temperature, level of supersaturation and whether or not agitation and/or seeding are used. For whey solutions, pre-crystallisation normally occurs between the evaporation and spray drying processing stages. Once the concentrate has been evaporated to between 50-60% total solids, it is flash-cooled to between 30-35°C and transferred into crystallisation tanks. These tanks are often equipped with stirrers to agitate the concentrate and cooling jackets to control the temperature. Once the tank is filled, lactose seeds (1 kg per 1000 kg concentrate) can also be added to initiate the crystallisation process. The tank is then gradually cooled, normally by approximately 2-3°C/h to less than 20°C (Písecký, 2012). This pre-crystallisation step can take anywhere from 6 to 24 h to complete, depending on the product requirements and composition. In industry, a refractometer is commonly used to track the changes in crystallinity of the solution over time. Once the product has reached the desired level of crystallinity the concentrate is pumped to the spray dryer to be dried.

#### 1.5.1.1.1 Extent of crystallisation

In theory, it would be desirable to crystallise 100% of the lactose present in the whey concentrate in order to prevent problems with stickiness. However, this is not possible due to the presence of impurities (e.g., proteins and minerals). Studies have shown that the addition of whey proteins to lactose solutions inhibited the growth of the lactose crystals (Gernigon et al., 2013; Mimouni et al., 2005). Conversely, the presence of whey proteins has also been shown to increase the rate of lactose crystal nucleation, as the proteins will bind water and therefore create areas of supersaturation (Gernigon et al., 2013; Mimouni et al., 2005). In a recent study by Ihli and Paterson (2015), the authors reported that oligosaccharides had a retarding effect on the nucleation and growth of  $\alpha$ -monohydrate crystals. Salts can also affect lactose crystallisation through their interaction with water molecules, which will affect the solubility of the lactose in solution (Huppertz and Gazi, 2016). Studies examining the effects of other additives commonly found in whey, such as lactates, phosphates and citrates, on lactose crystallisation have found that they can also



accelerate crystal growth (Gernigon et al., 2013; Smart, 1988). The influence of lactic acid and calcium on lactose crystallisation will be discussed in detail in a later (see Section 1.5.1.2.2).

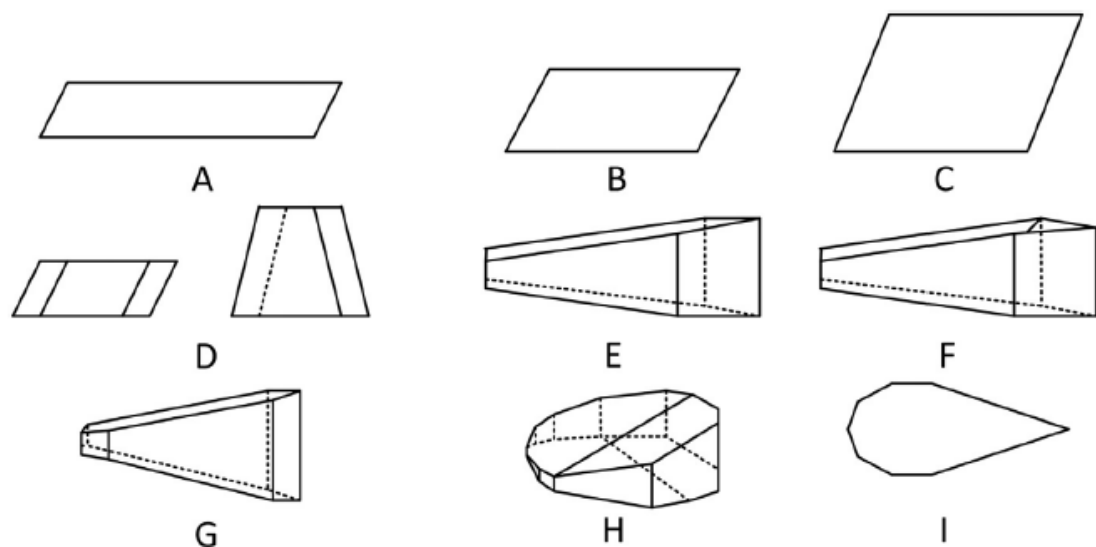
Although it is not possible to crystallise all the lactose in whey solutions, the degree of crystallinity is still an important factor in determining the stability of the subsequent powder. Studies have shown that pre-crystallisation of lactose may not be effective at protecting against sticking if the lactose present has not reached a sufficient level of crystallinity. For example, in a study by Hogan and O'Callaghan (2010) investigating the stickiness behaviour of dairy powders with varying protein/lactose contents, the authors observed that pre-crystallisation of the lactose in the skim milk/permeate powder (lactose content 74% w/w) did not confer any increased stability against sticking, when compared to the powders that contained predominantly amorphous lactose. The authors hypothesised that this was because the lactose in the powder was only approximately 68% crystalline, and therefore the coverage of amorphous lactose at the surface may have meant that the powder particles behaved similarly to those containing predominantly amorphous lactose. Similarly, Bronlund and Paterson (2004) showed that the presence of even small amounts of amorphous lactose on the surface of lactose crystals can significantly increase the extent of the moisture sorbed by the powder. For this reason, commercial whey and whey permeate powders typically contain between 75-80% crystalline lactose.

#### 1.5.1.1.2 Crystal form and shape

In an aqueous solution, lactose is present in both  $\alpha$  and  $\beta$  crystalline forms. These forms exist in a reversible equilibrium and the conversion of one form to another is known as mutarotation. Mutarotation is a reversible reaction and is highly temperature dependent. As the  $\alpha$  form is less soluble than the  $\beta$  form at a given temperature, the  $\alpha$  form will reach the point of supersaturation before the  $\beta$  form, and will result in the formation of  $\alpha$ -lactose monohydrate crystals (Westergaard, 2010). Therefore, in the dairy industry, under normal processing conditions, the most

commonly found crystalline form of lactose is the  $\alpha$ -lactose monohydrate form (Huppertz and Gazi, 2016). The  $\alpha$ -lactose monohydrate crystals have one molecule of water per molecule of lactose incorporated into their structure and are the most stable crystalline form. In order for these crystals to form, the crystallisation conditions must be so that crystallisation occurs slowly and sufficient moisture is present. At temperatures greater than 93.5°C, anhydrous  $\beta$ -lactose crystals will form. These crystals contain no water molecules (anhydride), are less stable and will convert to the  $\alpha$ -lactose form over time if sufficient moisture is present (Huppertz and Gazi, 2016).

Lactose crystals can exist in many different shapes (habits) depending on the conditions during crystallisation, which determine the growth rate of the different faces of the crystal, hence influencing its final shape (Fig. 1.4). An early study by Herrington (1934) determined that the level of supersaturation of the solution is the primary factor governing the shape of crystals during growth. The supersaturation level is highly temperature dependent, therefore different crystal habits will form based on the cooling rate used during crystallisation. For example, tomahawk-shaped



**Figure 1.4** Lactose crystal habits. Taken from Paterson (2017). A: prism (fast growth), B: prism (slow growth), C: diamond, D: pyramid, E+F: tomahawk, G: ‘fully developed’ tomahawk, H: 13 face crystal, I: profile view of H.

crystals normally form during slow evaporation/crystallisation conditions, whereas fast evaporation leads to higher levels of supersaturation and crystals with more needle-like morphologies (Parimaladevi and Srinivasan, 2014). Furthermore, minor components sometimes found in whey and permeate, such as oligosaccharides, have also been shown to affect the shape of  $\alpha$ -monohydrate crystals through their incorporation into the crystal lattice (Ihli and Paterson, 2015).

#### 1.5.1.2 Processing of acid whey

Processing of acid whey is considerably more challenging compared to the majority of other whey types due to its high content of lactic acid (LA) and calcium (Ca). The presence of LA and Ca can cause a number of undesirable side effects for dairy processors, such as salt formation during evaporation and increased stickiness of the powder during spray drying. Because of these undesirable effects, some studies have investigated ways to reduce levels of LA during acid whey production. For example, Chandrapala et al. (2017) examined the feasibility of various combinations of NF and nano diafiltration (NDF) for the removal of LA from acid whey and found that with a combination of pH adjustments and NF, they could achieve an overall reduction in LA of  $\sim 66\%$ . However, when minerals are also present, issues with fouling of the filtration membranes may also arise due to the effects of the salts on the protein-protein interactions, increasing the overall particle size (Nishanthi et al., 2017b). It should also be noted that many of the studies conducted on LA and Ca are often conducted on simple mixtures of lactose, water and LA and/or Ca. In reality, acid whey is a much more complex, multi-component solution; therefore these simple mixtures may not be fully representative of the interactions occurring during acid whey processing.

##### 1.5.1.2.1 Precipitation of salts

The first challenge that is commonly encountered during the processing of acid whey is the formation/precipitation of salts. LA and Ca can co-precipitate to form calcium lactate salts, which can increase the viscosity of the acid whey solution (Mimouni et al., 2007). Furthermore, Ca can also participate in the formation of salts with

phosphorus, to form  $\text{Ca}_3(\text{PO}_4)_2$  complexes (Písecký, 2012; Písecký, 2005). This problem is usually encountered during the evaporation step, causing deposits to build up on the tubes of the evaporator, damaging the equipment and impacting the final powder quality. One way of avoiding or minimising this issue is to put the concentrate through an ion-exchange or heat precipitation step before evaporation in order to remove/dissolve the minerals (Písecký, 2005).

#### 1.5.1.2.2 Lactose pre-crystallisation

Various studies (Chandrapala et al., 2016; Saffari and Langrish, 2014; Wijayasinghe et al., 2015; Wijayasinghe et al., 2016) have examined the influence of the presence of LA and/or Ca on lactose crystallisation. They reported that the presence and ratio of LA to Ca can significantly influence the crystallisation of lactose due to the effects on lactose solubility and diffusion (Wijayasinghe et al., 2015; Wijayasinghe et al., 2016). LA will interact with water in lactose solutions, leading to the formation of a strong hydration layer consisting of LA and  $\text{H}_3\text{O}^+$  ions around the lactose molecules, restricting the mobility of the water molecules and hindering the crystallisation of the lactose (Wijayasinghe et al., 2015). It is also thought that the presence of Ca in LA/lactose solutions can further strengthen this hydration layer due to the strong ion-dipole reactions that occur between Ca and water molecules (Wijayasinghe et al., 2016). The presence and ratio of LA to Ca will therefore affect crystallisation outputs such as crystal yield and size (Chandrapala et al., 2016). It is clear from these studies that the interactions between Ca, LA and lactose are very complex and still not fully understood.

#### 1.5.1.2.3 Effect on glass transition

Lactic acid is highly hygroscopic and has a low  $T_g$  and can therefore act as a plasticiser in an amorphous system. Studies have shown that the presence of LA in high-lactose powders will decrease the overall  $T_g$  of the lactose, leading to issues with stickiness and caking (Chandrapala and Vasiljevic, 2017; Saffari and Langrish, 2014; Shrestha et al., 2006; Wijayasinghe et al., 2016). However, Wijayasinghe et al. (2016) reported that the addition of Ca alone to a lactose solution increases the overall  $T_g$ , and when

LA and Ca are present in combination, the effect of the Ca on the  $T_g$  actually dominates that of the LA. Furthermore, the overall yield of spray-dried lactose powders decreases significantly with increasing LA concentration, which is likely due to the higher amount of powder sticking to dryer walls etc. (Chandrapala and Vasiljevic, 2017; Saffari and Langrish, 2014). Saffari and Langrish (2014) also demonstrated that the addition of WPI (5% w/w) to lactose/LA solutions can increase the overall powder yield, presumably due to the protective effect of protein against sticking.

### 1.5.1.3 Effect of spray drying on powder particles

#### 1.5.1.3.1. Surface composition

Stickiness is a surface related phenomenon and is therefore likely to be more closely related to the surface rather than bulk composition of powder particles. Many studies (Foerster et al., 2016, Nijdam and Langrish, 2006; Shrestha et al., 2007) have compared the surface and bulk compositions of various dairy powders and have shown that the surface composition of a particle can differ significantly from the bulk. Protein and fat tend to be over-represented at the surface, whereas lactose is normally underrepresented. Furthermore, of all of the milk components, fat appears to show the greatest extent of migration to the surface (Shrestha et al., 2007). Studies have found the fat content at the surface of SMP, which generally contains approximately 1% fat in the bulk, to be anywhere from 8% (Nijdam and Langrish, 2006), through 12% (Shrestha et al., 2007), to 18% (Kim et al., 2002). Nijdam and Langrish (2006) also showed that very small changes in the bulk fat content of a powder (for relatively low concentrations 0-5% fat) can significantly affect fat distribution at the surface. In contrast, Shrestha et al. (2007) observed very little change in the protein coverage at the surface ( $\pm 4\%$ ) when the protein in the bulk of the powder was increased from 9 to 34%. This is most likely due to the position of the different milk components at the particle surface. For example, studies have shown that fat is present as a thin film at the outermost layer at the surface and proteins are generally located directly underneath this layer of fat (Foerster et al.,

2016; Kim et al., 2002). This thin layer of fat would explain why changing the protein content of the bulk does not appear to affect the amount of protein at the surface.

#### 1.5.1.3.1.1. Fat at the surface of powder particles

As previously discussed (Section 4.2.1), the dominant presence of fat at the surface is significant to dairy producers as it can impact the stickiness of the powder. Foerster et al. (2016) reported that it is the atomisation stage (and not the subsequent drying stage) that is responsible for the component segregation and surface predominance of fat in dairy powders. Foerster et al. (2016) suggest that this over-representation of fat is primarily due to emulsion film disintegration caused by the shear stress imposed during atomisation along the oil–water interfaces of lipid globules, and possibly further enhanced by subsequent migration of fat to the surface during drying due to the low diffusivity of fat globules. In the same study, fat accumulation at the particle surface was also found to be independent of the type of atomisation used during drying. During the production of spray dried dairy emulsions, the type of fat used can also influence the amount of fat at the surface of the particle, with sunflower oil showing significantly higher (9%) surface fat coverage compared to milk fat (O'Neill et al., 2019). In the same study, O'Neill et al. (2019), the authors also showed that differences exist in the fatty acid profiles of the fats at different locations (surface, inner, and encapsulated) of the particle, with more C:16 and C18 and less C18:1 and C18:2 in the inner fat, compared to the surface and encapsulated fat. Furthermore, this would suggest that the presence of one or more double bonds effects the migration of fat during particle formation.

#### 1.5.1.3.1.2 Factors influencing surface composition

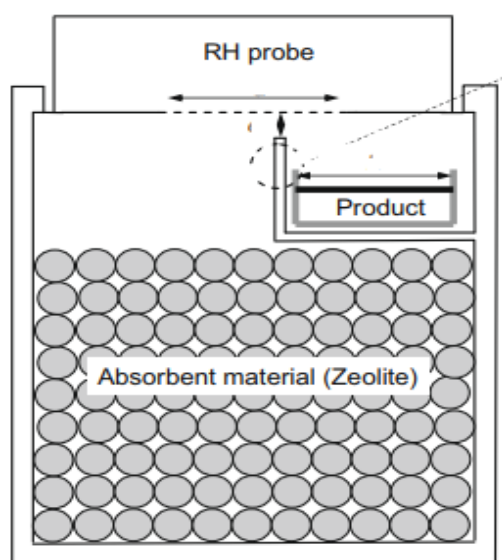
A number of different theories have been proposed to explain the mechanisms responsible for the distribution of milk components to the particle surface during spray drying, including differences in components surface activity, diffusivity and solubility (Foerster et al., 2016). However, the surface composition of a particle can also be affected by external factors, such as the conditions used during spray drying. For example, higher spray-drying temperatures can favour the migration of lactose

to the surface over protein (Kim et al., 2009; Nijdam and Langrish, 2006). Increasing the solids content of the feed has been shown to decrease surface fat coverage in SMP, and correspondingly increase lactose coverage (Kim et al., 2009). Kim et al. (2009) also examined the effect of particle size on surface composition of SMP but did not find any significant differences in surface composition between the various size fractions. However, the particle size range examined in the study was quite small (0-90  $\mu\text{m}$ ) and is not necessarily representative of the particle size distribution (PSD) seen in industrially-produced powders. In a subsequent study by Foerster et al. (2016), the authors found that protein migration to the surface was more distinct in larger droplets, however, this protein was hidden under the layer of fat on the outermost surface of the particle. The authors also reported that further enrichment of protein towards the surface region occurred during the drying stage. Although some studies have investigated the influence of surface fat on stickiness behaviour, there has been very little research carried out on the direct influence of the surface composition on the stickiness of different dairy powders.

#### 1.5.1.4 Optimisation of spray drying parameters

Spray drying is an important method for the dehydration and preservation of many dairy products, but it can be challenging to optimise due to the complex interrelationships between feed composition, drying parameters and dryer design variables. Hence, one of the only ways for dairy processors to determine the effects of altering drying parameters on the final product is to run a series of time consuming and expensive trials. For this reason, new methods are now being developed with the aim of determining the optimal spray drying parameters (inlet/outlet temperature, flow rate, etc.) that will result in maximum drying efficiency for individual dairy concentrates, while also avoiding undesirable side effects, such as stickiness. One such method is the drying by desorption method developed by Schuck et al. (2009). This method uses a desorption technique to determine the moisture transfer kinetics (ratio of bound to unbound moisture) in the sample during drying. The sample is placed into the small compartment of the cell, while the larger compartment is filled with absorbent material and a relative humidity sensor is

placed on top of the cell (Fig. 1.5). A vapour pressure gradient is created in the cell and water transfer takes place from the sample to the absorbent material. The drying information, along with dryer specifications and desired product parameters, can then be entered into the accompanying SD<sup>2</sup>P software to give the optimal drying parameters for that individual concentrate. This method has significant economic importance for dairy producers, as it can not only be used to maximise the efficiency of the dryer, it can also help to improve the physical characteristics of the final powder. One limitation of this method is that it does not take into account the risk of stickiness development during drying. For this reason, Zhu et al. (2011) developed a new method, based on this desorption technique, to determine the dry  $T_g$  of a concentrate. The authors examined the relationship between concentrate evaporation rate, solid content, viscosity and  $T_g$ , and developed an equation for the prediction of the dry  $T_g$  of a concentrate using this information (solids content, evaporation rate and viscosity). The dry  $T_g$  values obtained from this desorption method were compared to the  $T_g$  values from DSC for four infant formulas and the



**Figure 1.5** Schematic representation of drying by desorption cell. Taken from Schuck et al. (2009).



predicted dry  $T_g$  values were found to be 18-30°C higher than those measured using DSC. The advantage of this method is that it is easy and fast for Industry to apply, as it is done on a wet concentrate. However, more work must be carried out in order to improve the accuracy of the  $T_g$  predictions.

#### 1.5.1.5 Other factors affecting stickiness during spray drying

##### 1.5.1.5.1 Humidity in air

It is well known that the final moisture content of a powder is closely related to the outlet air temperature of the spray drier (Písecký, 2012). The higher the outlet temperature of the drier, the lower the moisture content of the powder (Písecký, 2012). However, in a recent study by Schuck et al. (2008), the authors demonstrated that this is not always the case. They showed that there is no direct relationship between outlet air temperature and powder moisture content. The only constant relationship they observed, from all of the spray drying parameters they examined, was between the moisture content of the powder and the relative humidity of the outlet air.

##### 1.5.1.5.2 Seasonal variation

As the air used in spray drying is generally heated ambient air, variations in the humidity of this air during different seasons must also be considered as it can affect the drying conditions, and ultimately the final moisture content of the powder. This will then have implications on the stickiness/caking behaviour of the powder. For example, warmer air during summer months will have higher humidity, meaning it will be holding more moisture than colder air. When this air is heated to the required inlet temperature, it will be holding more moisture and will therefore reduce the drying capacity of the drier. Trying to combat this issue by increasing the inlet temperature will only result in more evaporation occurring within the drier, which will raise the outlet air humidity and ultimately increase the final moisture content of the powder. An increase in the relative humidity of the ambient air can also lead to an increase in energy consumption and a decrease in the thermal efficiency of the drier (Kajiyama and Park, 2010). It is therefore not efficient to run spray dryers at the

same conditions throughout the year. The most effective way to avoid problems with stickiness, and maximise the drier efficiency, is through inlet air dehumidification, as this allows for the reduction and constant control of the humidity of the air supply to the drier (Nielsen, 2017). This will also result in a reduction in the humidity of the outlet air, which will reduce the final moisture content of the powder.

## 1.5.2 Stickiness during storage (caking)

### 1.5.2.1 Introduction to caking

Caking can be described as the undesirable clumping/agglomerating of powder particles resulting in the formation of lumps of varying size and hardness during the storage of powders. It negatively impacts the quality of dairy powders by impairing their functionality, leading to economic losses for the producer. Caking is closely related to stickiness, as both are surface-related phenomena that are strongly influenced by the physical changes that occur during the transition of an amorphous material from a higher to a lower viscosity state. There are two distinct differences between both phenomena; the time dependency and whether or not the particles are in motion. Stickiness usually occurs quite quickly during powder drying (seconds to minutes), whereas caking is a much slower process that can occur after weeks or months of storage. Furthermore, stickiness occurs between moving powder particles and/or equipment surfaces, while caking occurs between stationary particles. The different mechanisms of caking can be more precisely described as amorphous caking, humidity caking and mechanical caking, and have recently been discussed in detail in a review by Carpin et al. (2016). A very simple and general explanation of the most common caking process in lactose powders, amorphous caking, can be described as follows; water absorption by amorphous lactose, increase in the molecular mobility of the system causing liquid bridging and particle agglomeration to occur, often followed by lactose crystallisation and irreversible consolidation of bridges to form a solid cake.

#### 1.5.2.1.1 Factors influencing caking

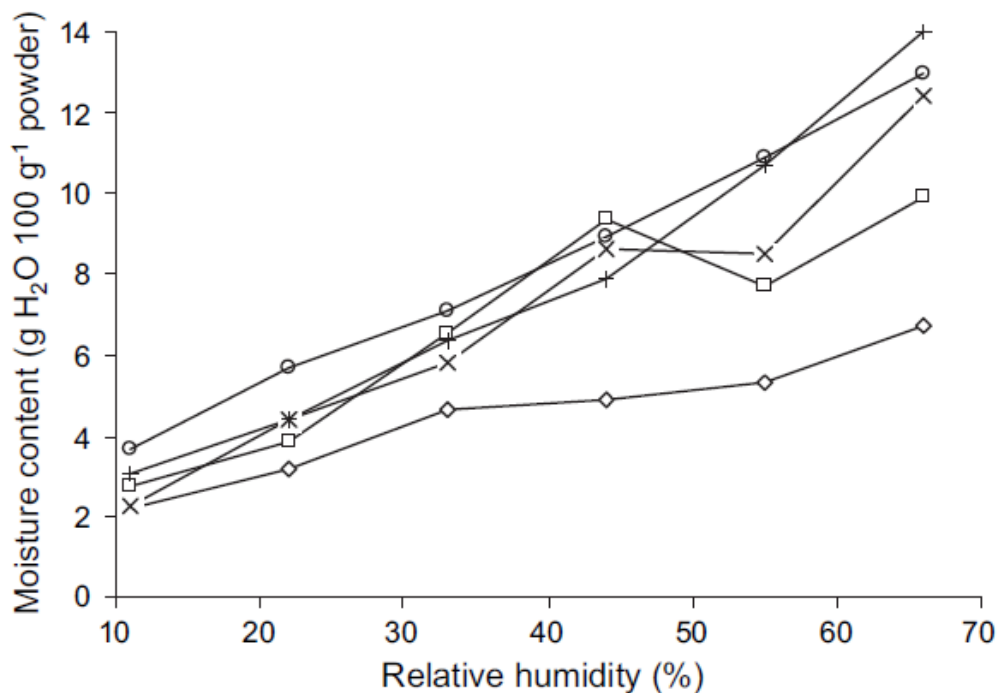
Because of the influence of the glass transition, many of the factors that influence the stickiness behaviour of a powder will also influence the tendency of a powder to form a cake. For example, moisture plays a critical role in both stickiness and caking due to its effect on the  $T_g$ . The hygroscopicity of a powder is therefore one of the primary indicators of whether or not a powder will cake during storage. Moreover, the amount of amorphous material present in the powder will influence caking as higher amorphous lactose contents will lead to increased moisture sorption (Listiohadi et al., 2005). Storage temperature also has a significant influence on caking, as increasing the temperature beyond the  $T_g$  will cause thermal plasticisation to occur in a process known as sintering. Similarly to stickiness, the greater the difference between the  $T_g$  and process/storage temperature ( $T - T_g$ ), the greater the extent of caking (Foster et al., 2006). Therefore, the RH and temperature conditions at which a powder is stored must be tightly controlled in order to avoid/minimise issues with caking (Aguilera et al., 1995). Surface fat content has also been shown to influence caking strength as liquid fat bridges between particles will crystallise and solidify when temperatures decrease to form strong bonds (Foster et al., 2005a). Studies by Carpin et al. (2017a) and Modugno et al. (2015) have also investigated the effect of particle size on caking and have found that lactose powders with smaller particle size distributions (PSD) have an increased tendency to cake, due to enhanced particle interactions.

#### 1.5.2.2 Moisture sorption

Water acts as a plasticiser to reduce the  $T_g$  and the overall stability of a powder. It is therefore necessary to determine the moisture sorption tendency of a powder in order to take the necessary measures to prevent stickiness/caking from occurring. The most common method for determining the water sorption behaviour in foods is through the use of moisture sorption isotherms, such as those shown in Fig. 1.6. Moisture sorption isotherms provide information on the water sorption capacity of a sample as a function of  $a_w$  at a constant temperature, and for dairy powders can be

good indicators of the amount of water that a powder is likely to sorb from the surrounding air. Powder hygroscopicity is a similar indicator, where a hygroscopicity classification (eg. slightly hygroscopic) is given to a powder to describe how likely it is to sorb moisture. Hygroscopicity can be defined as the final moisture content of a powder after it has been subjected to a humid environment under normal conditions (Schuck et al., 2012), and corresponds to a certain point on the moisture sorption isotherm.

Various studies (Berlin, 1968; Foster, 2005) have used moisture sorption isotherms to show that the sorption behaviour of dairy powders, such as SMP, can be successfully predicted from the contribution of the primary milk components of that powder. These mainly include carbohydrates, proteins and other smaller hygroscopic components, such as minerals. For example, amorphous lactose is extremely hygroscopic and will readily sorb moisture from the surrounding air (Ibach and Kind, 2007). Increasing the amount of amorphous lactose in dairy powders has been shown to significantly increase moisture absorption (Shrestha et al., 2007). In contrast, crystalline lactose is non-hygroscopic and absorbs very little moisture (Bronlund and Paterson, 2004). Proteins generally adsorb moisture at lower RHs (Schuck et al., 2012). For example, Silalai and Roos (2010) reported that at low  $a_w$  values ( $< 0.33$ ), water sorption increased with increasing protein content for a variety of milk protein concentrate (MPC) powders. Moisture sorption/hygroscopicity can also be influenced by particle size, as smaller particles will have more surface area available for sorption to occur. Smaller particles have been shown to absorb more moisture in both crystalline lactose (Carpin et al., 2017a) and sucrose powders (Mathlouthi and Roge, 2003). This could be due to the larger SSA or a higher amount of impurities, such as hygroscopic salts, often found in the smaller size fractions (Carpin et al., 2017b).



**Figure 1.6** Graph showing typical moisture sorption isotherms of a variety of dairy powders: Skim milk/permeate blend (15% protein) (◇), Skim milk/permeate blend (25% protein) (□), skim milk powder (SMP) (x), milk protein concentrate (55% protein) (+) and milk protein concentrate (80% protein) (o). Taken from Hogan and O'Callaghan (2010).

#### 1.5.2.2.1 Time-dependent crystallisation during storage

The stability of milk powders during storage is dependent on the physic state of the primary compounds. In the case of powders such as whey permeates, it is primarily the physical state of the lactose that will determine the storage stability, due to the influence of the glass transition. For example, powders containing high amounts of amorphous lactose will undergo time-dependent crystallisation if subjected to temperature and RH conditions that exceed the  $T_g$  during storage. This phenomenon is generally undesirable as it may lead to the formation of solid cakes in the powder.

The crystallisation process will begin with the amorphous lactose absorbing moisture from the surrounding air due to its hygroscopic nature, causing an increase in molecular mobility. The lactose molecules will then re-arrange themselves from their

unorganised amorphous structure into structured crystalline arrays. As the lactose crystallises, water of crystallisation will be released, which will be characterised as a loss of adsorbed water (Bronlund and Paterson, 2004; Jouppila and Roos, 1994a; Jouppila and Roos, 1994b; Silalai and Roos, 2010). However, in powders with sufficient protein contents, the water released during crystallisation may be re-absorbed by the proteins present (Haque and Roos, 2004a; Hogan and O'Callaghan, 2010; Ibach and Kind, 2007; Shrestha et al., 2007). There are a wide variety of factors that influence the time-dependent crystallisation of amorphous lactose. During exposure to humid conditions, higher temperature and relative humidity conditions lead to faster crystallisation rates (Ibach and Kind, 2007). Increasing the amorphous lactose content of a powder has also been shown to increase the moisture sorption (Bronlund and Paterson, 2004) and decrease the RH at which time-dependent crystallisation begins (Haque and Roos, 2004a; Hogan and O'Callaghan, 2010; Shrestha et al., 2007). Various studies (Chandrapala and Vasiljevic, 2017; Haque and Roos, 2004a; Haque and Roos, 2004b; Hogan and O'Callaghan, 2010; Ibach and Kind, 2007; Jouppila and Roos, 1994a; Silalai and Roos, 2010,) have examined the time-dependent crystallisation of amorphous lactose in dairy powders and have shown that the milk components present, such as proteins and salts, delay crystallisation compared to pure lactose systems.

#### 1.5.2.2.2 Methods for determining moisture sorption/hygroscopicity

Moisture sorption isotherms are most commonly determined using the static gravimetric method described by Stitt (1958), in which dried samples are placed in desiccators containing saturated salt solutions in temperature controlled conditions. This subjects the samples to a constant temperature and RH environment. The samples are weighed periodically until equilibrium is reached. The data obtained from these experiments are often fitted to a mathematical model, such as the Guggenheim, Anderson, de Boer (GAB) model, which is widely used in the dairy industry for modelling sorption isotherms (Bronlund and Paterson, 2004; Foster et al., 2005b; Jouppila and Roos, 1994b). The advantage of this static method is that it is very simple and does not require specialised equipment. Hygroscopicity is

calculated in a very similar way, subjecting the sample to a certain RH (normally 75%), and weighing the sample until an equilibrium is reached. This information, along with the moisture content of the sample, is then entered into a formula to produce a value for the hygroscopicity (Schuck et al., 2012). It should also be noted that there are more automated techniques available to measure moisture sorption isotherms. One such method is dynamic vapour sorption (DVS), which has been used to measure the moisture sorption in a wide range of dairy powders, including spray dried lactose/protein powders (Kelly et al., 2016), dairy powders with different vegetable oils (Kelly et al., 2014), MPC powders (Kelly et al., 2015), WMP (Murrieta-Pazos et al., 2011) and SMP (Murrieta-Pazos et al., 2011).

## **1.6. Methods to determine stickiness**

A wide variety of techniques have been developed and studied to determine the stickiness behaviour of dairy powders (Table 1.2). An important factor that needs to be considered for these techniques is the time dependence of stickiness. Techniques that estimate stickiness development over shorter time scales (seconds or minutes) would be more representative of the changes that occur during spray drying, as opposed to those that track changes in stickiness over longer time scales. Furthermore, it should be noted that all these methods are on a lab-scale, and therefore the stickiness information gathered for individual powders may not be directly comparable to what is occurring within the spray drier. A short summary of the most relevant methods for stickiness determination in dairy powders and some of their main advantages/disadvantages will be discussed in the subsequent sections.

### **1.6.1 Direct measurements**

The direct measurement techniques are based on the measurement of a property of the powder, such as the viscosity or resistance to shear, and can be further classified as conventional, pneumatic or *in situ* techniques. The primary objective of these techniques is to gradually increase the humidity of a sample in order to determine

the stickiness, as the glass transition changes from a solid to a more liquid state. However, it should be noted that during spray drying the opposite is actually occurring, as moisture is desorbed and the glass transition is changing from a liquid to a solid state (Huppertz and Gazi, 2016). While direct methods provide good indications of the conditions leading to stickiness development, they are not direct indications of how stickiness will occur in the spray drier due to differences in particle trajectories, air velocities etc.

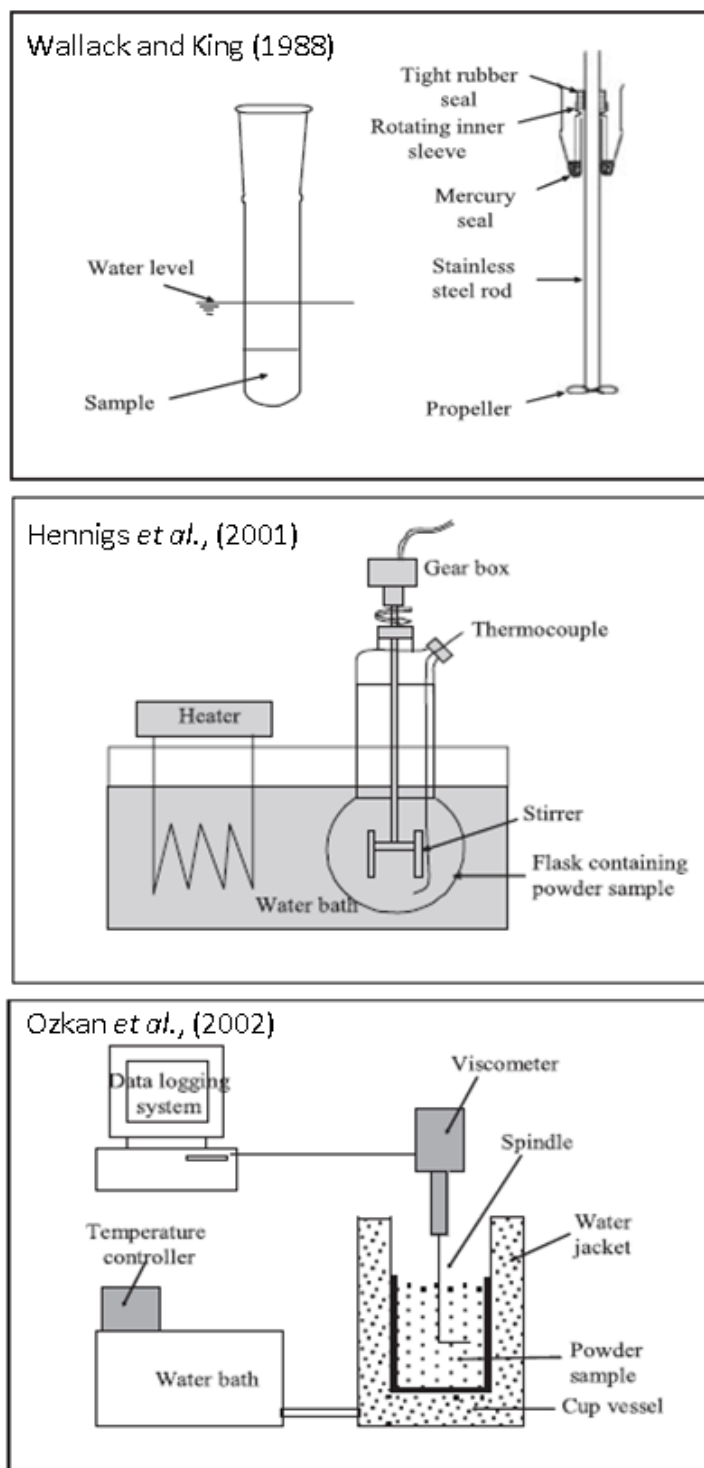
**Table 1.2** Overview of various techniques used for stickiness determination of dairy powders. Modified from O’Callaghan and Hogan (2013).

Technique	Conditioned air	Controlled particle velocity	Reference
Wall deposition	No	No	Ozmen and Langrish (2003)
Sticky-point tester	No	No	Hennigs et al., (2001) Ozkan et al., (2002)
Cyclone stickiness test	Yes	No	Boonyai et al. (2002) Boonyai et al., (2006)
Fluidisation/ Fluid bed	Yes	No	Hogan et al., (2009) Hogan et al., (2010) Murti et al., (2010)
Particle gun	Yes	Yes	Chatterjee (2004) Paterson et al., (2007) Zuo et al., (2007) Murti et al., (2009)
Blow test	Yes	No	Brooks (2000) Paterson et al., (2001)



### 1.6.1.1 Conventional methods

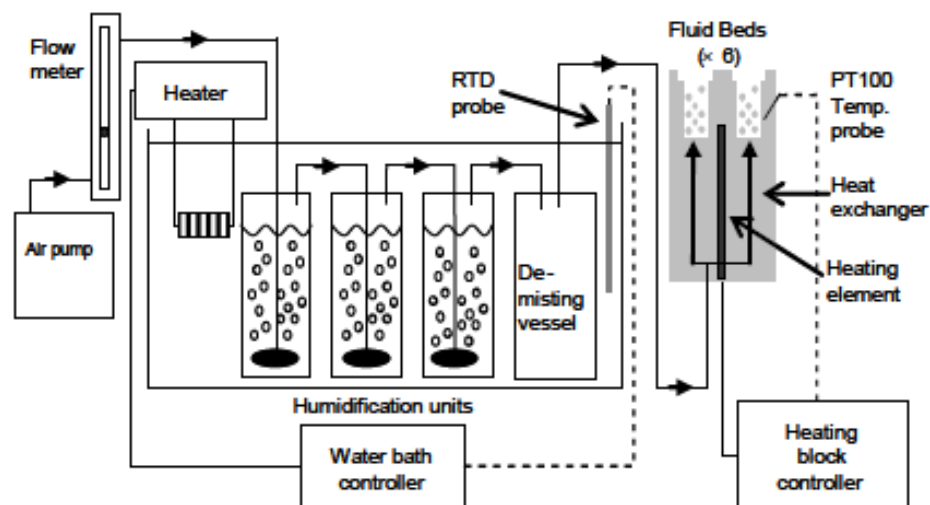
One of the first stickiness measurement techniques was a thermo-mechanical test developed by Lazar et al. (1956), which was conducted on spray-dried tomato powder (Fig. 1.7). The technique involved placing a sample of known moisture content into a test tube which was submerged in a heating medium. The temperature of the sample was increased at a specific rate during the course of the experiment, and an impeller placed in the sample and turned manually until there was a sharp increase in the force required to stir the sample, which represented the change in viscosity of the sample and therefore the sticking point temperature. This technique has been modified and improved over the years and is now also used for stickiness determination of dairy powders (Fig. 1.7). Brennan et al. (1971) introduced a motor-driven propeller and later, Hennigs et al. (2001) designed a sealed sample flask and added measurement of electric resistance output from the stirrer. A disadvantage of the method used by Hennigs et al. (2001) was that a void could form in the powder, causing the powder to stick to the outer particles without successfully determining the sticky-point temperature. A similar viscometer-based technique was developed by Özkan et al. (2002) to measure the stickiness behaviour of SMP and WMP. This technique involved placing the powder sample into a sample cup that was contained inside a temperature-controlled jacket. After the sample had equilibrated to the surrounding temperature an L-shaped propeller was placed in the centre of the sample and a viscometer was used to measure the torque required to stir the sample. Similar to the method developed by Lazar et al. (1956), the sticking point temperature was determined as the point where a sharp increase in the torque occurred. One limitation that is common to all the methods described above is that they are static methods, and therefore do not accurately represent the conditions within the spray drier.



**Figure 1.7** Schematic diagram showing the evolution of the sticky-point measurement device first created by Lazar *et al.* (1956). Modified from Boonyai *et al.* (2004).

### 1.6.1.2. Pneumatic methods

Pneumatic methods, such as the fluidisation or cyclone stickiness tests, involve the use of an air stream that comes into contact with the powder, and therefore more closely represent the stickiness behaviour of a powder during spray drying, compared to the static methods discussed in Section 1.6.1.1. Hogan et al. (2009) and Murti et al., (2010) both designed miniature fluidised bed systems to characterise the stickiness of a variety of dairy powders. The design used by Hogan et al. (2009) can be seen in Fig. 1.8. This method involved suspending powder samples in an air stream that had been humidified by passing it through vessels containing water that are submerged in a water bath. The RH of the air is then increased by increasing the temperature of the water bath at a constant rate. The sticking point is determined as the temperature at which the powder ceases fluidising and air channels develop in the powder. An advantage of this fluidisation method is that it measures both cohesion and adhesion, as it allows collision of individual particles against one another while also simulating impaction of particles against the chamber wall. However, it should be noted that the results from this fluidisation method cannot be directly compared to the conditions during spray drying due to the differences particle velocities. Boonyai et al. (2006) reported using a cyclone stickiness test to measure the sticking point temperature of various food powders, including whey powder. The apparatus consists of a cyclone test chamber, where the stickiness behaviour is observed, along with air heaters, a humidification chamber and a dehumidification tube. A pre-conditioning step is required before testing the sample in order to stabilise the conditions in the humidification chamber. After equilibration, a small amount of sample (~1 g) is introduced into the top of the cyclone chamber. The sample is carried along in the air stream which moves in a rotary motion. After a few minutes sticky behaviour can be observed as the particles begin to stick to one another and the chamber wall.



**Figure 1.8** Schematic diagram of fluidisation apparatus for stickiness determination of dairy powders. Taken from Hogan et al. (2009).

Paterson et al. (2001) reported using the blow test method for measuring the stickiness of powders (Fig. 1.9). This method measures the air flow rate (L/min) required to blow a channel into a bed of powder. The air used to blow through the powder bed was pre-conditioned to a desired temperature and RH, but unlike other methods was kept constant throughout the course of the experiment. This method may be subject to some error due to imperfections in the bed surface and fluctuations in the conditions during the experiment. It should also be noted that while this method has been used to measure 'stickiness' in some studies (Paterson et al., 2001; Paterson et al., 2005), it is perhaps more accurate to categorise this as a method for measuring the caking strength of powder due to the static nature of the particles in the bed of powder.

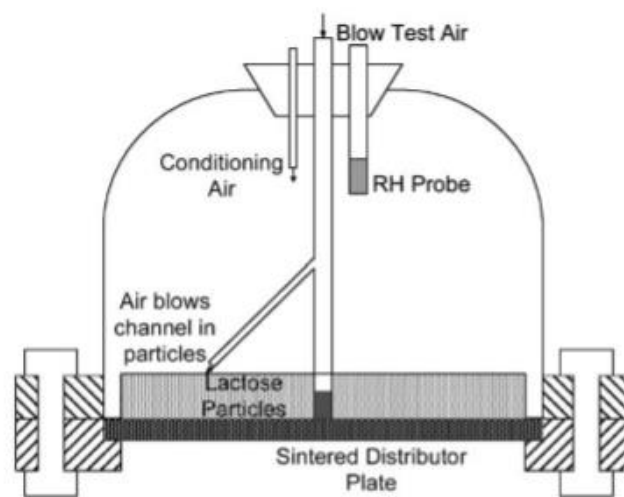
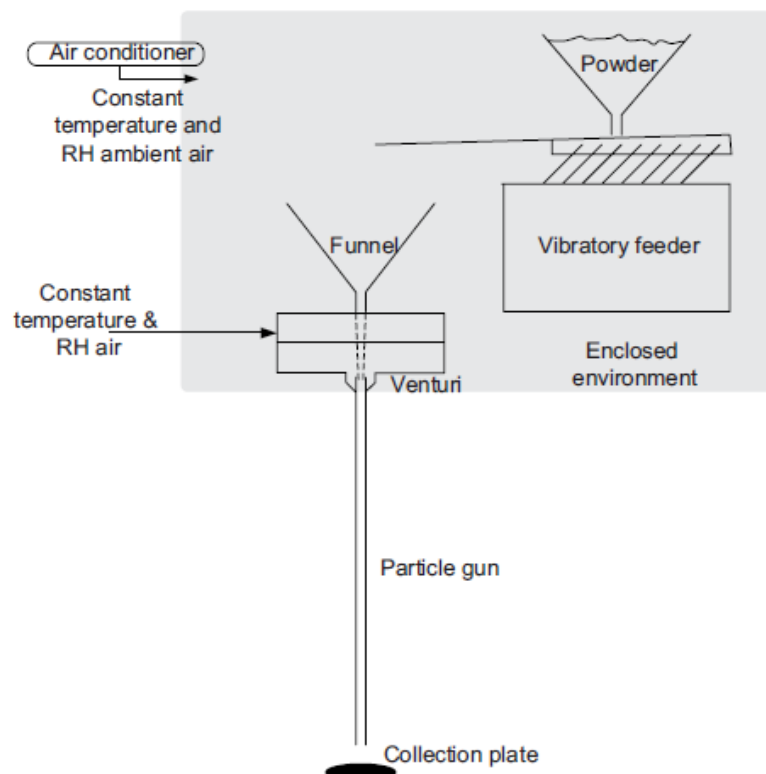


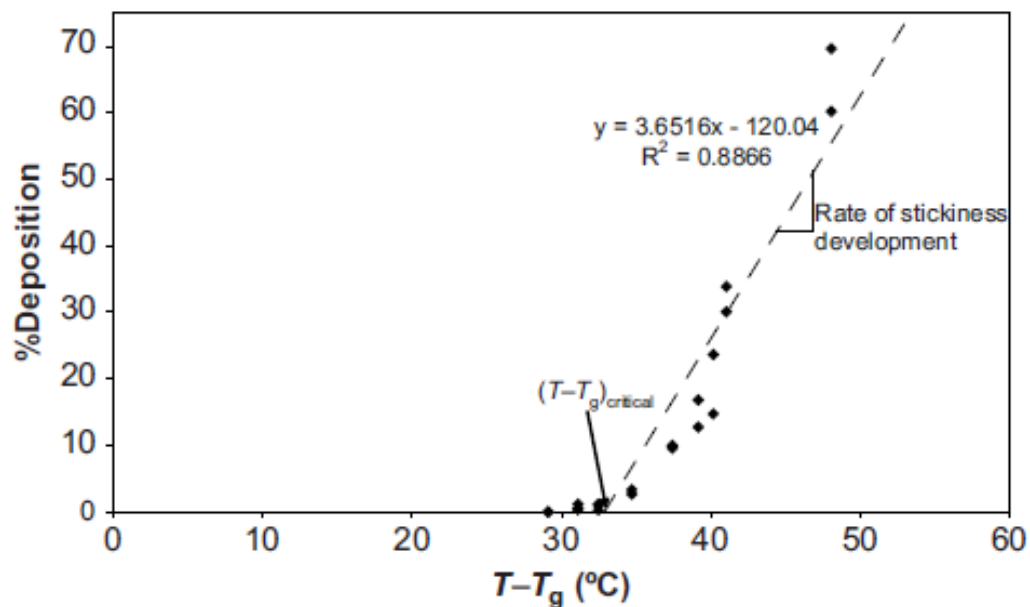
Fig. 2. Schematic diagram of blow tester used in this work.

**Figure 1.9** Schematic diagram of the blow test method used for measuring powder stickiness. Taken from Paterson et al. (2005).



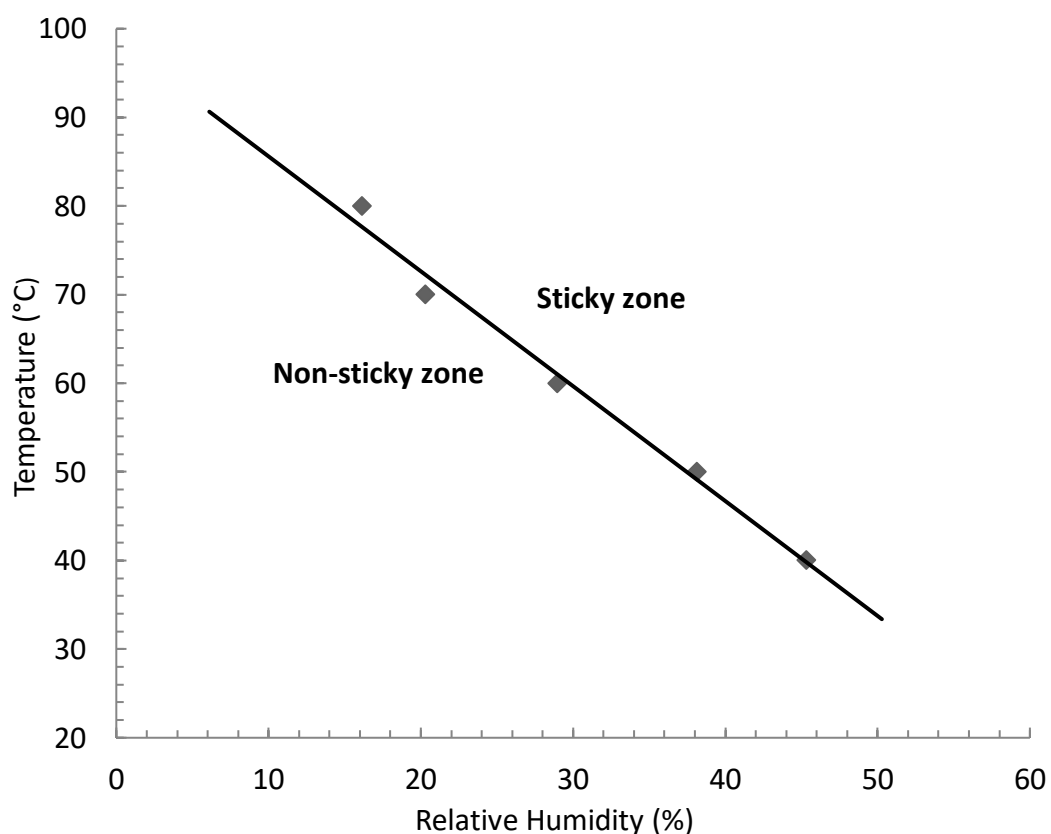
**Figure 1.10** Schematic diagram of the particle gun (including modifications) used for measuring powder stickiness. Taken from Murti et al. (2009)

Chatterjee (2004), and later Zuo et al. (2007), Paterson et al. (2007) and Murti et al. (2009), used a particle gun apparatus to determine the stickiness of powders when they collide with equipment surfaces (adhesion) (Fig. 1.10). The temperature and humidity of the air stream can be controlled using a combination of heating elements and air pressure regulators. A venturi is used to accelerate the air through the particle gun. A fixed amount of powder (25 g) is dropped into a glass funnel at the top of the vortex chamber and travels through the 103 cm long perspex tube at a velocity of 20 m/s. When the powder exits the tube it adheres to a stainless steel plate and the plate is weighed to determine the mass of powder that has adhered to the plate. This apparatus works under the assumption that the surface layer of the particles instantly equilibrates with the contacting air, and that this small layer is sufficient to cause stickiness in powders. Some advantages of this method compared to other stickiness techniques are that the higher air velocities are more representative of those used during spray drying and that it also accounts for particle contact with the drier walls. Fig. 1.11 shows a plot for % deposition for SMP, where the temperature was kept constant (77°C) and the RH was gradually increased (Murti et al., 2009).



**Figure 1.11** Deposition (%) of skim milk powder (SMP) using the particle gun apparatus. Taken from Murti et al. (2009).

In order for the techniques mentioned above to be useful to dairy processors, it must be possible to relate the experimental information back to the operating conditions used during spray drying. For this reason, the results obtained for the many of these methods can be represented as a point on a graph of air temperature (representing the outlet temperature of a spray dryer) as a function of RH. If the stickiness behaviour has been tested at a variety of temperatures or RHs, these points can be graphed and connected to form a curve, known as a 'stickiness curve' (Fig. 1.12). The area below the curve represents the temperature and RH conditions where powders would not be expected to cause problems with stickiness. This stickiness curve provides operators with useful information on the safe operating conditions for a given powder.



**Figure 1.12** Typical stickiness curve for skim milk powder (SMP), showing 'sticky' and 'non-sticky' zones. Modified from O'Donoghue et al. (2019).

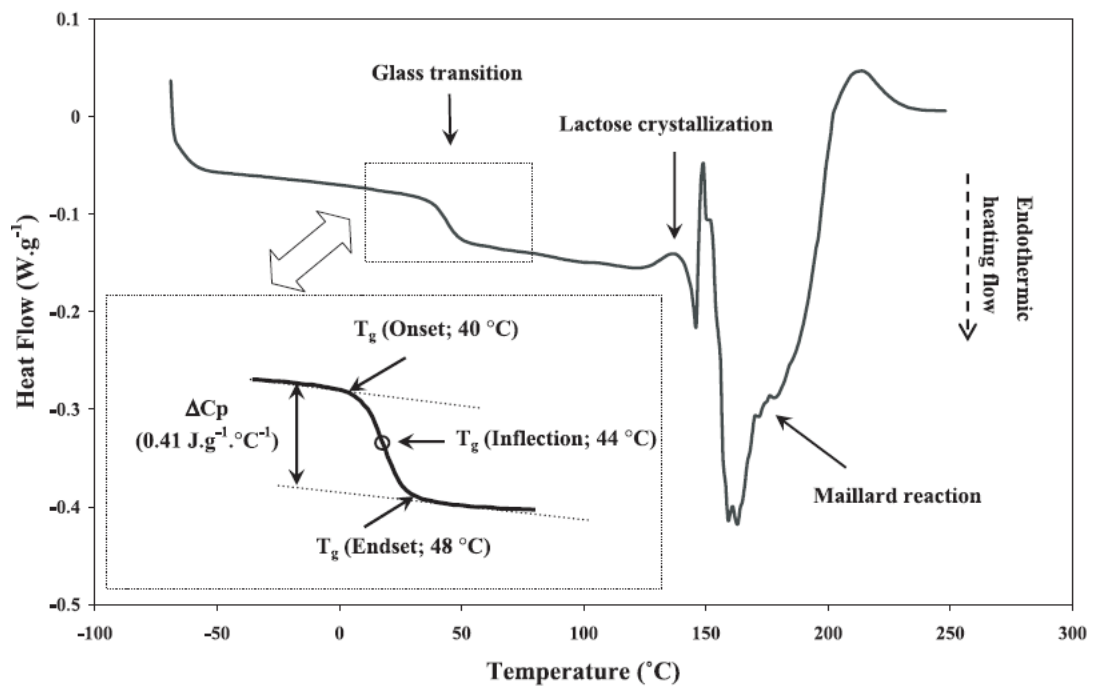
### 1.6.2 Indirect methods

Indirect methods measure changes in a physical property of the material that can be indirectly correlated to stickiness. For example, during the glass transition, changes occur in the heat capacity as well as the viscoelastic and dielectric properties of the material. Hence, there are a wide range of techniques that can be used to measure such changes. Two of the most commonly used methods in the dairy industry are differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). A brief summary of each method is given below.

#### 1.6.2.1 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a thermo-analytical technique that is commonly used to determine the glass transition temperature ( $T_g$ ) of foods, including dairy powders (Haque and Roos, 2004a; Haque and Roos, 2004b; Jouppila and Roos, 1994a; Maidannyk and Roos, 2017; Ozmen and Langrish, 2002; Silalai and Roos, 2010; Silalai and Roos, 2011b). This method measures the change in specific heat that occurs during phase transitions by comparing the sample to a reference sample of a known specific heat capacity. Both samples are heated over a defined time and are maintained at the same temperature throughout the experiment. The amount of heat required to maintain the sample at the same temperature as the reference can then be measured. For example, if a solid melts to a liquid it will absorb heat and therefore require more heat in order to maintain it at the same temperature as the reference sample. Similarly, if the sample undergoes a phase change from liquid to solid state, such as during crystallisation, the reaction will release heat and less heat will be required to raise the sample temperature. These changes can then be represented on a graph of heat flow as a function of temperature, known as a DSC thermogram (Fig 1.13). However, it should be noted that these phase transitions do not occur at a precise temperature, but rather over a region with three defined parameters; the onset ( $T_{gi}$ ), midpoint ( $T_{gm}$ ) and endset ( $T_{ge}$ ) temperature. It is therefore important when referring to  $T_g$  values in the literature to specify which  $T_g$  value (i.e., onset, midpoint or endset) is being reported.

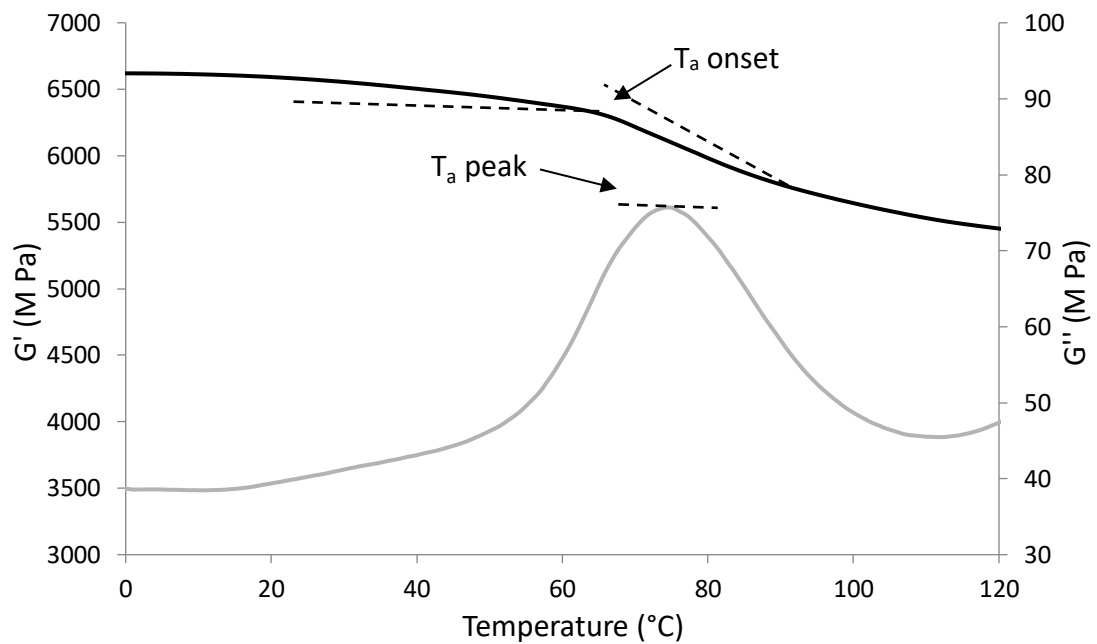




**Figure 1.13** Differential scanning Calorimetry (DSC) thermogram showing glass transition in non-crystalline whey powder at 0.22  $a_w$ . Taken from Schuck et al. (2005).

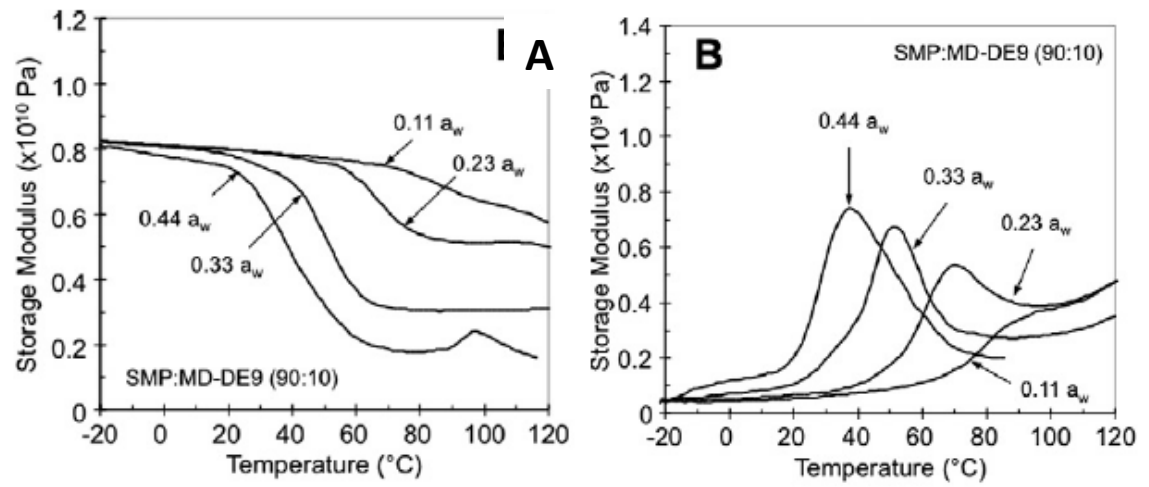
#### 1.6.2.2 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) is a technique used to measure changes in the viscoelastic behaviour of a material. This method involves subjecting the sample to a sinusoidal force and measuring the resulting strain in the material, given as the storage ( $E'$ ) and loss ( $E''$ ) moduli. The storage modulus describes the amount of energy stored in the sample, i.e., the elasticity, whereas the loss modulus describes the energy lost from the sample and is an indication of viscosity. During the glass transition, as the material 'relaxes' into a stable (crystalline) state, there will be a considerable decrease in storage modulus and a corresponding increase in the loss modulus. Theoretical values, known as  $\alpha$ -relaxation temperatures ( $T_a$ ), can then be determined from the changes in the storage and loss moduli. For example, the  $T_a$  onset is calculated from the onset of the decrease in the storage modulus and the  $T_a$  peak is determined as the peak of the curve of the loss modulus (Fig. 1.14). These  $\alpha$ -relaxations normally occur above the  $T_g$  and can be generally related to changes in



**Figure 1.14.** Graph showing  $T_a$  onset (storage modulus) and  $T_a$  peak (loss modulus) values of a whey protein concentrate powder using dynamic mechanical analysis. Taken from O'Donoghue et al. (unpublished data).

stickiness behaviour, as both are associated with changes in viscoelastic behaviour. Silalai and Roos (2011b) used this DMA method to determine the mechanical  $\alpha$ -relaxations of a range of SMP-maltodextrin powders (Fig. 1.15). They compared these results to the results obtained from a sticky point tester, modified from the design by Lazar et al. (1956), and found that the  $\alpha$ -relaxation results were good indicators for stickiness development. However, these mechanical relaxations are dependent on the frequency used (Silalai and Roos, 2010), hence a range of frequencies is normally analysed. This method may therefore provide a potential option for measuring the stickiness of powders that cannot be measured using the direct methods outlined above, e.g., powders with very high fat contents.



**Figure 1.15** Graphs showing storage (A) and loss (B) moduli of a skim milk powder (SMP)/maltodextrin mix at different water activities. Modified from Silalai and Roos (2011b).

## Objectives

The main objective of the research reported in this thesis was to develop a deeper understanding of the compositional and analytical factors affecting stickiness development in dairy powders. The work presented was performed with a view to minimise the occurrence and severity of stickiness during the spray drying of lactose-containing dairy powders, and also to investigate a new method which could potentially provide dairy powder technologists with a more mechanistic understanding of stickiness development.

The aims of the research are as follows:

- To characterise the bulk and surface compositions of various size fractions of different lactose-containing dairy powders, and to investigate whether differences exist in the stickiness behaviour and hygroscopicity of these fractions.
- To compare the  $\alpha$ -relaxation temperatures, derived from the storage and loss modulus using DMA, of a variety of whey protein concentrate (WPC) powders with the results from other more established methods for stickiness characterisation and glass transition determination, such as the fluidisation method and differential scanning calorimetry, respectively.

## **Chapter 2: Influence of particle size on the physicochemical properties and stickiness of dairy powders**

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**Abstract**

This study investigated the compositional and physicochemical properties of different whey permeate (WPP), demineralised whey (DWP) and skim milk powder (SMP) size fractions. Bulk composition of WPP and DWP was significantly ( $P < 0.05$ ) influenced by powder particle size; smaller particles had higher protein and lower lactose contents. Microscopic observations showed that WPP and DWP contained both larger lactose crystals and smaller amorphous particles. Bulk composition of SMP did not vary with particle size. Surface composition of the smallest SMP fraction ( $<75\text{ }\mu\text{m}$ ) showed significantly lower protein (-9%) and higher fat (+5%) coverage compared to non-fractionated powders. For all powders, smaller particles were more susceptible to sticking. Hygroscopicity of SMP was not affected by particle size; hygroscopicity of semi-crystalline powders was inversely related to particle size. This study provides insights into differences between size fractions of dairy powders, which can potentially impact the sticking/caking behaviour of fine particles during processing.

## 2.1 Introduction

Stickiness and hygroscopicity of powders, especially those with high carbohydrate contents, are major challenges for the dairy industry, particularly during the spray drying process. Sticky powders can become deposited on the walls of the spray drier and block bag-houses and cyclones, decreasing process efficiency, product yield and quality. Stickiness is a surface phenomenon that occurs when the surface of powder particle reaches a critical viscosity (between  $10^6$  and  $10^8$  Pa.s), which allows for the formation of liquid bridges, causing cohesion between colliding particles and/or adhesion to equipment surfaces (Downton et al., 1982). The viscosity of the particle surface is governed by many factors, such as moisture content, the physical state of lactose and temperature (Downton et al., 1982; Hogan et al., 2009). A wide variety of techniques have been developed over the years in order to determine the conditions at which powders becomes sticky, with sticking temperature ( $T$ ) usually reported as a function of relative humidity (RH) (Boonyai et al., 2006; Hogan et al., 2009; Intipunya et al., 2009; Lazar et al., 1956; Murti et al., 2009; Paterson et al., 2005; Paterson, et al., 2007).

Powders containing large amounts of amorphous lactose are particularly susceptible to sticking as amorphous carbohydrates are thermodynamically unstable and undergo a phase transition from a 'glassy' to 'rubbery' state around a critical temperature, known as the glass transition temperature ( $T_g$ ). This transition is also highly dependent on humidity due to the plasticisation effect of water, which lowers  $T_g$  (Haque and Roos, 2004a; Jouppila and Roos, 1994a; Ozmen and Langrish, 2002; Roos and Karel, 1991c). As the  $T_g$  is exceeded, the molecular mobility of the system will increase and the particle surface viscosity will decrease, leading to the onset of sticking (Foster et al., 2006). As a consequence of this, stickiness is commonly encountered during spray drying due to high temperature and RH conditions. The temperature difference between the  $T_g$  and sticking point temperature, known as the  $T-T_g$ , has been extensively studied and is often used to describe the sticking behaviour of dairy powders (Hennigs et al., 2001; Hogan et al., 2009; Murti et al., 2009; Ozmen & Langrish, 2002; Paterson et al., 2005; Paterson et al., 2007). It should

be noted that the  $T-T_g$  can vary depending on the measurement technique used (Paterson et al., 2005; Paterson et al., 2007) and the composition of the powder (Hogan et al., 2009).  $T-T_g$  values reported for SMP vary from 14-22 °C, using a thermo-mechanical test (Ozmen and Langrish, 2002), 23.3 °C, using a direct stirrer-type technique (Hennigs et al., 2001), 25-34 °C, using a variety of fluidised bed apparatus (Hogan and O'Callaghan, 2010; Hogan et al., 2009; Murti et al., 2010) to 31.5-33.6 °C using a particle gun (Murti et al., 2009; Murti et al., 2010).

In order to minimise processing and product quality challenges associated with stickiness, feeds containing large amounts of lactose, such as whey and whey permeates, are often subjected to a pre-crystallisation step before drying in order to convert the majority of the amorphous lactose (typically 75-80%) into the more stable, crystalline form. However, it is not possible to fully crystallise all of the dissolved lactose. Resulting powders are therefore semi-crystalline in nature, as they contain both lactose crystals and a proportion of amorphous lactose (~20-25% of total lactose), in addition to other milk components (Bansal and Bhandari, 2016). These components differ in diffusivity and molecular weight and therefore may not be distributed evenly between size fractions (Meerdink and van't Riet, 1995), leading to differences in stickiness behaviour.

Particle size is thought to play a role in powder stickiness as it has been shown to have a significant effect on the cohesive and adhesive strength of dairy powders (Rennie et al., 1999). As previously mentioned, it is commonly observed in industrial settings that the fines exiting the spray dryer with the exhaust air often stick to the surfaces of the air filtration systems (e.g., cyclones and bag houses). However, to date, very little research has been carried out investigating the effect of particle size on the stickiness of dairy powders. As part of a study by Hogan et al. (2009), the authors examined the differences in stickiness behaviour between two SMP samples of different particle sizes ( $D[4,3]$  values of 130 and 61  $\mu\text{m}$ ) but did not find any significant difference between the stickiness of the two size fractions.



The hygroscopicity of a dairy powder describes its final moisture content after exposure to humid air at a constant temperature. Hygroscopicity is closely linked with stickiness, as increased moisture content increases the rate of stickiness development (Murti et al., 2009). Various studies (such as Carpin et al., 2017a and Haque and Roos, 2004b) have investigated the influence of particle size on water absorption by different dairy powders. Haque and Roos (2004b) examined the differences in water uptake of coarse and fine amorphous lactose/protein powders and found that the fine particles absorbed slightly more water than the coarse powder particles at relative vapour pressures (RVP)  $\leq 33.2\%$ . Similarly, Carpin et al. (2017a) found that for crystalline lactose powders, smaller particles showed an increase in water absorption compared to larger particles at RHs  $> 50\%$ . Rogé and Mathlouthi (2000) also showed the same effect of particle size on water uptake for crystalline sucrose.

Many studies (Kim et al., 2002; 2005a; 2009; Nijdam and Langrish, 2006; Shrestha et al., 2007) have compared the bulk and surface compositions of various dairy powders and found that the proportions of protein, fat and lactose on the surface of the particle can be significantly different from those in the bulk of the powder. While such observations are useful, information on the relationship between particle size and surface composition is limited. Kim et al. (2009) sieved a commercial SMP and examined the surface composition of various size fractions but found no significant effect of particle size on surface composition. However, the range of particle sizes examined in the study by Kim et al. (2009) was very small (between 0-90  $\mu\text{m}$ ) and therefore not representative of the range of particle sizes typically found in industrially produced powders. To the author's knowledge, there are no published studies available on the relationships between particle size and surface composition of semi-crystalline dairy powders, such as whey permeates.

The objectives of this study were to characterise the bulk and surface compositions of various size fractions within different dairy powders, and to investigate whether differences exist in the stickiness behaviour and hygroscopicity of these fractions. In particular, the stickiness behaviour of the smaller size fractions, or fines, was of

interest, as excessive stickiness in this fraction can be a limiting factor during spray drying.

## **2. 2 Materials and methods**

### **2.2.1. Materials**

Demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP) were supplied by local dairy ingredient companies. Saturated salt solutions magnesium chloride ( $\text{MgCl}_2$ ), potassium carbonate ( $\text{K}_2\text{CO}_3$ ) and sodium chloride ( $\text{NaCl}$ ) were purchased from Sigma Aldrich (Co. Wicklow, Ireland).

### **2.2.2. Powder fractionation**

Powders were sieved using a laboratory test sieve shaker (Octagon 200 test sieve shaker, Endecotts Ltd, London, UK) using three different sieve sizes (250, 150 and 75  $\mu\text{m}$ ). The powders were sieved in batches of 300 g at amplitude 7 for 4 min. The powder in each sieve was then weighed in order to determine the proportion of each size fraction in the original powder. Two batches of the WPP and four batches of the DWP and SMP were sieved in total. All fractions were well mixed, stored in airtight plastic containers and analysed within 2 months.

### **2.2.3. Particle size distribution**

The particle size distributions (PSD) of each powder fraction were measured by laser light scattering using a Mastersizer 3000 (Malvern Instruments Ltd., UK), equipped with an Aero S dry powder dispersion unit. Particle size measurements were recorded as the volume mean diameter ( $D[4,3]$ ).

### **2.2.4. Powder composition**

Total moisture was determined by Karl-Fischer titration using a 784 KFP Titrino auto-titration system (Metrohm AG, Herisau, Switzerland) as described by GEA (2006).

Protein determination was carried out using a LECO Nitrogen Analyser FP-638 (LECO Corporation, Michigan, USA), using a nitrogen-to-protein conversion factor of 6.38. Non-protein nitrogen (NPN) content was measured using the Kjeldahl method, after precipitation of intact proteins using trichloroacetic acid (TCA). In the absence of an accurate method to measure whey:casein ratio in heat treated SMP, the ratio was taken to be 20:80. Lactose content was measured using a lactose assay kit (Megazyme K-LOLAC, Ireland). It should be noted that there was an insufficient amount of powder to test the  $x < 75 \mu\text{m}$  fraction of the DWP for lactose and NPN, so a simple linear regression was carried out to extrapolate the data. For the SMP fractions, lactose content was assumed to be the same as the original powder. Fat content was analysed by Röse-Gottlieb (IDF, 1987). Ash content was determined after overnight incineration in a muffle furnace at  $550^{\circ}\text{C}$ . Water activity ( $a_w$ ) was determined using a Novasina Labmaster.aw (Novatron Scientific Ltd., UK). Free moisture was determined by oven drying at  $86^{\circ}\text{C}$  for 6 h.

#### 2.2.5. Lactose crystallinity

Lactose crystallinity (%) was calculated according to the formula described by Schuck & Dolivet (2002):

$$\frac{BWL.19}{L} \times 100$$

where BWL is the bound water content in the lactose ( $\text{g kg}^{-1}$ ) and L is the lactose content ( $\text{g kg}^{-1}$ ).

The BWL was calculated according to the following formula:  
 $BWL = TW - FW - (0.0152.CC) - (0.005.WPC) - (0.0155.MSSC)$   
 where TW: total water content ( $\text{g kg}^{-1}$ ), FW: free water content ( $\text{g kg}^{-1}$ ), CC: casein content ( $\text{g kg}^{-1}$ ), WPC: whey protein content ( $\text{g kg}^{-1}$ ) and MSSC: milk salt solution content ( $\text{g kg}^{-1}$ ).

### 2.2.6. Scanning electron microscopy

Scanning electron microscopy (SEM) was carried out with a field-emission scanning electron microscope (FE-SEM, Zeiss Supra 40 VP Gemini, Darmstadt, Germany) at 2.00 kV. Powder samples were mounted on double-sided carbon tape attached to SEM stubs and lightly coated with chromium (Emitech K575X, Ashford, UK) prior to analysis. Images were taken at 500 X magnification.

### 2.2.7. Stickiness

Powder stickiness was determined using a fluidisation technique previously described by Hogan et al. (2009). Stickiness curves were generated by plotting the air (dry bulb) temperature against the RH (calculated from the saturated air temperature and absolute humidity) at which fluidisation ceased. To determine the effect of surface fat on stickiness behaviour, stickiness curves were generated for powders washed in petroleum ether, as described by Kim et al. (2005a).

### 2.2.8. Powder fluidisation velocity

Minimum air fluidisation velocities were determined using an Anton Paar MCR 302 rheometer (Graz, Austria), equipped with a powder cell attachment. An 80 mL bed of powder was subjected to an increasing air flow (from 0–5 L min<sup>-1</sup>) and the minimum air velocity required to fluidise the powder was determined by studying the pressure drop across the powder bed and dividing by the cross-sectional area. The air used to fluidise the powders in the powder cell was in compliance with ISO 8573.1, class 1.3.1, with a dew point of -20°C and 0.8 kg moisture/kg dry air. All analysis was conducted at room temperature (~20°C). The air velocity (m s<sup>-1</sup>) passing through each fluid bed in the stickiness apparatus was determined by dividing the total air flow rate (3.5 L min<sup>-1</sup>) by 5 (for each fluid bed) and then dividing by the cross sectional area of one fluid bed.

### 2.2.9. Differential scanning calorimetry

Powders were analysed without pre-equilibration under controlled atmosphere conditions. The water activity ( $a_w$ ) of the different size fractions varied slightly from 0.34-0.36, 0.28-0.36 and 0.30-0.31 for the DWP, WPP and SMP, respectively. Glass transitions in the three powders were measured using a Q2000 differential scanning calorimeter (DSC; TA Instruments, Crawley, UK) as described by Murphy et al. (2015). Hermetically sealed differential scanning calorimetry (DSC) aluminium pans, containing between 14-24 mg of powder, were heated in a nitrogen purged environment using the following method; heating from 0 to 60°C at 5°C min<sup>-1</sup>, cooling from 60°C to -10°C at 10°C min<sup>-1</sup>, and finally heating at 5°C to an end temperature of 100°C. The  $T_g$  midpoint values were calculated from the second heating cycle and all analyses were completed in at least duplicate.  $T-T_g$  values were calculated as the difference between sticky point temperature (T) and  $T_g$ , and represent a single point between both curves at the  $a_w$  of the powder. For powders washed with petroleum ether  $T_g$  values of the original powder were used.

### 2.2.10. Hygroscopicity

Powder hygroscopicity was measured according to the method described by Schuck et al. (2012). Powder samples (~2 g) were placed in desiccators over saturated salts of K<sub>2</sub>CO<sub>3</sub> at 43% RH. The samples were equilibrated and weighed at regular intervals until a constant weight was observed.

Hygroscopicity was calculated using the following formula:

$$\frac{((w_2 - w_1 - w_0) \times 1000) + (w_1 \times M)}{(w_2 - w_0) \times 10}$$

Where  $w_0$  = vial weight (g),  $w_1$  = sample weight (g),  $w_2$  = weight of vial after equilibration (g), M = % free moisture (% w/w)

### 2.2.11. Surface analysis of powders

X-ray photoelectron spectroscopy (XPS) measurements were made using a Kratos AXIS Ultra spectrometer (Kratos Analytical Ltd., Manchester, UK). The relative amounts of protein, fat and lactose at the powder surface were determined using a matrix formula created from the elemental compositions of the pure milk components, according to the method described by Faldt et al. (1993). It should be noted that after calculation the WPP tested in this study gave a slight negative surface fat value for all size fractions. Considering that the fat content of the powder was negligible ( $\sim 0.1\%$  w/w), the equations were adjusted in order to remove fat; fat content of WPP surfaces were considered to be “not determined” (N.D.).

### 2.2.12. Statistical analysis

All analysis was carried out in at least duplicate. Statistical analysis was carried out by subjecting data sets to one-way ANOVA with a least significant difference (LSD) test using SPSS for Windows Regression Models (IBM Ireland Ltd., Dublin, Ireland) statistical analysis package. A level of confidence of  $P \leq 0.05$  was used.

## 2.3 Results

**Table 2.1** Proportion (% w/w) of each size fraction in original demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP), separated using 250  $\mu\text{m}$ , 150  $\mu\text{m}$  and 75  $\mu\text{m}$  sieves.

	<b>x &gt; 250 <math>\mu\text{m}</math></b>	<b>250 &gt; x &gt; 150 <math>\mu\text{m}</math></b>	<b>150 &gt; x &gt; 75 <math>\mu\text{m}</math></b>	<b>x &lt; 75 <math>\mu\text{m}</math></b>
	<b>%</b>	<b>%</b>	<b>%</b>	<b>%</b>
DWP (n = 4)	6.52 $\pm$ 2.27	69.2 $\pm$ 3.74	22.6 $\pm$ 5.33	1.65 $\pm$ 0.62
WPP (n = 2)	5.36 $\pm$ 1.49	21.1 $\pm$ 1.79	66.0 $\pm$ 3.77	7.60 $\pm$ 0.50
SMP (n = 4)	1.42 $\pm$ 0.07	38.1 $\pm$ 1.12	54.0 $\pm$ 1.85	6.53 $\pm$ 0.79

### 2.3.1. Powder characterisation

#### 2.3.1.1 Particle size fractions and bulk composition of powders

The proportion of each size fraction in the original powders is shown in Table 2.1. In all three powders studied the majority of particles were between 250 and 75  $\mu\text{m}$ . However, in DWP the majority of powder particles were between 250 and 150  $\mu\text{m}$ , compared to WPP and SMP, which mostly contained particles in the range 150 - 75  $\mu\text{m}$ . Bulk compositional differences were observed between the various size fractions of the original semi-crystalline powders (Table 2.2). For DWP and WPP, smaller particles contained higher levels of protein and lower levels of lactose compared to larger particles. The same trend was not seen for SMP, which showed no significant variation ( $P > 0.05$ ) in bulk composition between size fractions. Mineral content of DWP and WPP was also significantly higher ( $P \leq 0.05$ ) in smaller size fractions. In a similar study by Carpin et al. (2017a), the authors also observed higher protein and mineral contents for smaller particles of crystalline lactose powder. The average non-protein nitrogen (NPN) content, expressed as a percentage of total nitrogen, was  $4.60 \pm 0.01$ ,  $13.5 \pm 2.29$  and  $35.6 \pm 10.6\%$  across all size fractions of SMP, DWP and WPP, respectively.

As expected, DWP and WPP contained a higher amount of lactose ( $80.2 \pm 1.27$  and  $87.3 \pm 0.83\%$ , respectively) compared to SMP ( $48.5 \pm 6.11\%$ ). The majority of lactose in DWP and WPP was in the crystalline form ( $\alpha$ -lactose monohydrate). This is a result of the pre-crystallisation step that occurs before spray drying, in which the majority of amorphous lactose present is converted into the more stable, crystalline form. However, for all size fractions studied, DWP contained higher levels of non-crystalline lactose compared to WPP. In WPP, the smaller particles contained much higher levels of amorphous lactose (40.1% of total lactose in  $x < 75 \mu\text{m}$  fraction) compared to larger particles (8.60% of total lactose in  $x > 250 \mu\text{m}$  fraction). A similar trend was also observed for DWP. Furthermore, representation of SMP crystallinity in terms of  $\alpha$ -lactose monohydrate is not ideal, as unlike during the manufacture of DWP and WPP, a pre-crystallisation step is not performed prior to drying; therefore any lactose crystals present may consist of mixtures of  $\alpha$ - and  $\beta$ -lactose (Jouppila and Roos,

1994a). Therefore, caution should be exercised when interpreting SMP crystallinity values (as  $\alpha$ -lactose monohydrate) from Table 2.2.

#### 2.3.1.2. Surface composition of powders

Surface compositions differed from bulk compositions in the three powders examined (Table 2.3). Protein and fat contents were higher at the particle surface, while lactose concentrations at the surface were lower than in the bulk. These findings are consistent with other studies in which it was also reported that protein and fat preferentially migrate to the surface of the particle during drying (Nijdam and Langrish, 2006; Shrestha et al., 2007).



**Table 2.2** Bulk composition of original and fractionated demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP).<sup>a</sup>

	Size fraction ( $\mu\text{m}$ )	True Protein <sup>b</sup> (% w/w)	Fat (% w/w)	Total Lactose (% w/w)	Ash (% w/w)	Total Moisture (% w/w)	Free Moisture (% w/w)	Crystalline Lactose <sup>c</sup> (% of Lactose)
DWP	Original	11.4 $\pm$ 0.28 <sup>a</sup>	1.11 $\pm$ 0.02 <sup>a</sup>	80.2 $\pm$ 1.27 <sup>a</sup>	0.70 $\pm$ 0.15 <sup>ac</sup>	4.93 $\pm$ 0.15 <sup>a</sup>	1.75 $\pm$ 0.01 <sup>a</sup>	73.8
	x > 250	8.23 $\pm$ 0.04 <sup>b</sup>	0.85 $\pm$ 0.00 <sup>b</sup>	88.3 $\pm$ 1.05 <sup>b</sup>	0.49 $\pm$ 0.15 <sup>ab</sup>	4.93 $\pm$ 0.06 <sup>a</sup>	1.34 $\pm$ 0.01 <sup>b</sup>	76.2
	250 > x > 150	10.8 $\pm$ 0.18 <sup>c</sup>	1.04 $\pm$ 0.01 <sup>c</sup>	79.4 $\pm$ 0.28 <sup>a</sup>	0.77 $\pm$ 0.10 <sup>ac</sup>	4.99 $\pm$ 0.22 <sup>a</sup>	1.71 $\pm$ 0.05 <sup>a</sup>	76.9
	150 > x > 75	11.8 $\pm$ 0.13 <sup>d</sup>	1.16 $\pm$ 0.00 <sup>d</sup>	75.4 $\pm$ 0.61 <sup>c</sup>	0.79 $\pm$ 0.01 <sup>c</sup>	5.10 $\pm$ 0.12 <sup>a</sup>	1.86 $\pm$ 0.10 <sup>a</sup>	79.9
	x < 75 <sup>d</sup>	21.4 $\pm$ 0.09 <sup>e</sup>	1.95 $\pm$ 0.03 <sup>e</sup>	71.6	1.43 $\pm$ 0.11 <sup>d</sup>	5.13 $\pm$ 0.08 <sup>a</sup>	3.10 $\pm$ 0.26 <sup>c</sup>	50.5
WPP	Original	3.52 $\pm$ 0.05 <sup>a</sup>	0.08 $\pm$ 0.01 <sup>a</sup>	87.3 $\pm$ 0.83 <sup>a</sup>	6.77 $\pm$ 0.03 <sup>a</sup>	5.63 $\pm$ 0.13 <sup>a</sup>	1.65 $\pm$ 0.00 <sup>a</sup>	84.0
	x > 250	0.54 $\pm$ 0.02 <sup>b</sup>	0.08 $\pm$ 0.01 <sup>a</sup>	99.2 $\pm$ 0.94 <sup>b</sup>	1.59 $\pm$ 0.02 <sup>b</sup>	5.18 $\pm$ 0.28 <sup>b</sup>	0.38 $\pm$ 0.00 <sup>b</sup>	91.4
	250 > x > 150	2.89 $\pm$ 0.07 <sup>c</sup>	0.11 $\pm$ 0.01 <sup>a</sup>	93.1 $\pm$ 3.19 <sup>c</sup>	5.89 $\pm$ 0.11 <sup>c</sup>	5.57 $\pm$ 0.12 <sup>a</sup>	1.46 $\pm$ 0.00 <sup>c</sup>	81.6
	150 > x > 75	3.47 $\pm$ 0.05 <sup>d</sup>	0.10 $\pm$ 0.05 <sup>a</sup>	83.7 $\pm$ 1.10 <sup>a</sup>	7.68 $\pm$ 0.01 <sup>d</sup>	5.63 $\pm$ 0.06 <sup>a</sup>	1.86 $\pm$ 0.01 <sup>d</sup>	82.4
	x < 75	6.01 $\pm$ 0.01 <sup>e</sup>	0.13 $\pm$ 0.01 <sup>a</sup>	70.5 $\pm$ 0.06 <sup>d</sup>	12.9 $\pm$ 0.12 <sup>e</sup>	5.59 $\pm$ 0.10 <sup>a</sup>	3.14 $\pm$ 0.00 <sup>e</sup>	59.9
SMP	Original	36.4 $\pm$ 0.56 <sup>a</sup>	1.06 $\pm$ 0.07 <sup>a</sup>	48.5 $\pm$ 6.11	7.31 $\pm$ 0.02 <sup>a</sup>	5.52 $\pm$ 0.14 <sup>a</sup>	5.05 $\pm$ 0.00 <sup>a</sup>	3.28
	x > 250 <sup>e</sup>	36.1 $\pm$ 0.03 <sup>a</sup>	0.94 $\pm$ 0.01 <sup>b</sup>	48.5 $\pm$ 6.11	7.19 $\pm$ 0.03 <sup>b</sup>	5.57 $\pm$ 0.13 <sup>a</sup>	5.04 $\pm$ 0.01 <sup>a</sup>	10.9
	250 > x > 150 <sup>e</sup>	36.3 $\pm$ 0.05 <sup>a</sup>	0.95 $\pm$ 0.02 <sup>b</sup>	48.5 $\pm$ 6.11	7.24 $\pm$ 0.01 <sup>bc</sup>	5.47 $\pm$ 0.02 <sup>a</sup>	5.12 $\pm$ 0.10 <sup>a</sup>	2.20
	150 > x > 75 <sup>e</sup>	36.4 $\pm$ 0.05 <sup>a</sup>	0.93 $\pm$ 0.02 <sup>b</sup>	48.5 $\pm$ 6.11	7.23 $\pm$ 0.03 <sup>bd</sup>	5.50 $\pm$ 0.04 <sup>a</sup>	5.07 $\pm$ 0.01 <sup>b</sup>	8.80
	x < 75 <sup>e</sup>	36.5 $\pm$ 0.06 <sup>a</sup>	1.00 $\pm$ 0.03 <sup>ab</sup>	48.5 $\pm$ 6.11	7.25 $\pm$ 0.03 <sup>cd</sup>	5.51 $\pm$ 0.03 <sup>a</sup>	5.13 $\pm$ 0.07 <sup>a</sup>	3.66

<sup>a</sup> For each powder, different superscript letters within the same column represent a significant difference ( $P \leq 0.05$ )<sup>b</sup> True protein = (Total nitrogen – Non-protein nitrogen) x 6.38<sup>c</sup> As  $\alpha$ -lactose monohydrate<sup>d</sup> Extrapolated value for non-protein nitrogen and lactose<sup>e</sup> Assumed lactose value

**Table 2.3** Surface composition of original and fractionated demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP), given in percentage protein, fat and lactose coverage.<sup>a b</sup>

	Size fraction ( $\mu\text{m}$ )	Crude Protein (% w/w)	Fat (% w/w)	Lactose (% w/w)
DWP	Original	41.2 $\pm$ 0.50 <sup>ac</sup>	28.4 $\pm$ 2.72 <sup>a</sup>	30.4 $\pm$ 2.16 <sup>a</sup>
	x > 250	42.3 $\pm$ 1.00 <sup>bc</sup>	28.3 $\pm$ 0.85 <sup>a</sup>	29.4 $\pm$ 0.21 <sup>a</sup>
	250 > x > 150	44.0 $\pm$ 0.50 <sup>b</sup>	26.7 $\pm$ 0.44 <sup>a</sup>	29.3 $\pm$ 0.93 <sup>a</sup>
	150 > x > 75	41.6 $\pm$ 1.00 <sup>ac</sup>	26.2 $\pm$ 3.51 <sup>a</sup>	32.1 $\pm$ 2.45 <sup>a</sup>
	x < 75	39.4 $\pm$ 1.00 <sup>a</sup>	27.9 $\pm$ 0.14 <sup>a</sup>	32.3 $\pm$ 0.84 <sup>a</sup>
WPP	Original	54.2 $\pm$ 0.00 <sup>a</sup>	n.d <sup>c</sup>	35.4 $\pm$ 0.25 <sup>a</sup>
	x > 250	45.8 $\pm$ 3.98 <sup>b</sup>	n.d <sup>c</sup>	36.5 $\pm$ 1.27 <sup>a</sup>
	250 > x > 150	54.6 $\pm$ 1.49 <sup>a</sup>	n.d <sup>c</sup>	36.5 $\pm$ 0.51 <sup>a</sup>
	150 > x > 75	51.8 $\pm$ 3.49 <sup>ab</sup>	n.d <sup>c</sup>	35.4 $\pm$ 0.76 <sup>a</sup>
	x < 75	49.7 $\pm$ 0.50 <sup>ab</sup>	n.d <sup>c</sup>	35.2 $\pm$ 1.01 <sup>a</sup>
SMP	Original	52.4 $\pm$ 0.98 <sup>a</sup>	9.56 $\pm$ 1.60 <sup>a</sup>	35.9 $\pm$ 0.56 <sup>a</sup>
	x > 250	47.6 $\pm$ 1.95 <sup>b</sup>	18.5 $\pm$ 3.25 <sup>b</sup>	32.5 $\pm$ 1.43 <sup>b</sup>
	250 > x > 150	47.6 $\pm$ 0.00 <sup>b</sup>	12.2 $\pm$ 0.84 <sup>ac</sup>	38.7 $\pm$ 0.98 <sup>ac</sup>
	150 > x > 75	47.2 $\pm$ 0.49 <sup>b</sup>	11.0 $\pm$ 1.76 <sup>ac</sup>	40.2 $\pm$ 1.13 <sup>c</sup>
	x < 75	43.8 $\pm$ 0.49 <sup>c</sup>	14.8 $\pm$ 1.20 <sup>bc</sup>	39.7 $\pm$ 1.76 <sup>cd</sup>

<sup>a</sup> For each powder, different superscript letters within the same column represent a significant difference ( $P \leq 0.05$ ).

<sup>b</sup> percentage coverage is on a dry basis

<sup>c</sup> n.d – not determined

Many studies have shown that the surface fat content of dairy powders is significantly higher than the bulk composition (Kim et al., 2009; Nijdam and Langrish, 2006). In the present study, fat coverage of the original SMP was found to be 9.56  $\pm$  1.60%, which is considerably higher than the 1.06  $\pm$  0.07% fat found in the bulk of the powder. Kim et al. (2009) reported a higher surface fat content of 18% for a

commercial SMP with a bulk composition of approximately 1% fat, whereas Nijdam and Langrish (2006) reported a surface fat content of approximately 8% for a SMP with 1.10% bulk fat content. Foerster et al. (2016) demonstrated that, for industrially spray-dried powders, it is the atomisation stage (and not the subsequent drying stage), which is the primary determinant of surface composition, and is responsible for overrepresentation of surface fat. It is thought that fat globules are ruptured during atomisation and are spread homogeneously over the droplet surface, creating a thin film of fat. At lower fat concentrations (between 0-5%) small changes in bulk fat content of the powder can also cause significant increases in the fat content at the surface (Nijdam and Langrish, 2006). This may have implications on powder stickiness and caking ability, as a higher fat content at the surface can potentially create a more cohesive particle and promote the formation of weak bridges between particles (Nijdam and Langrish, 2006).

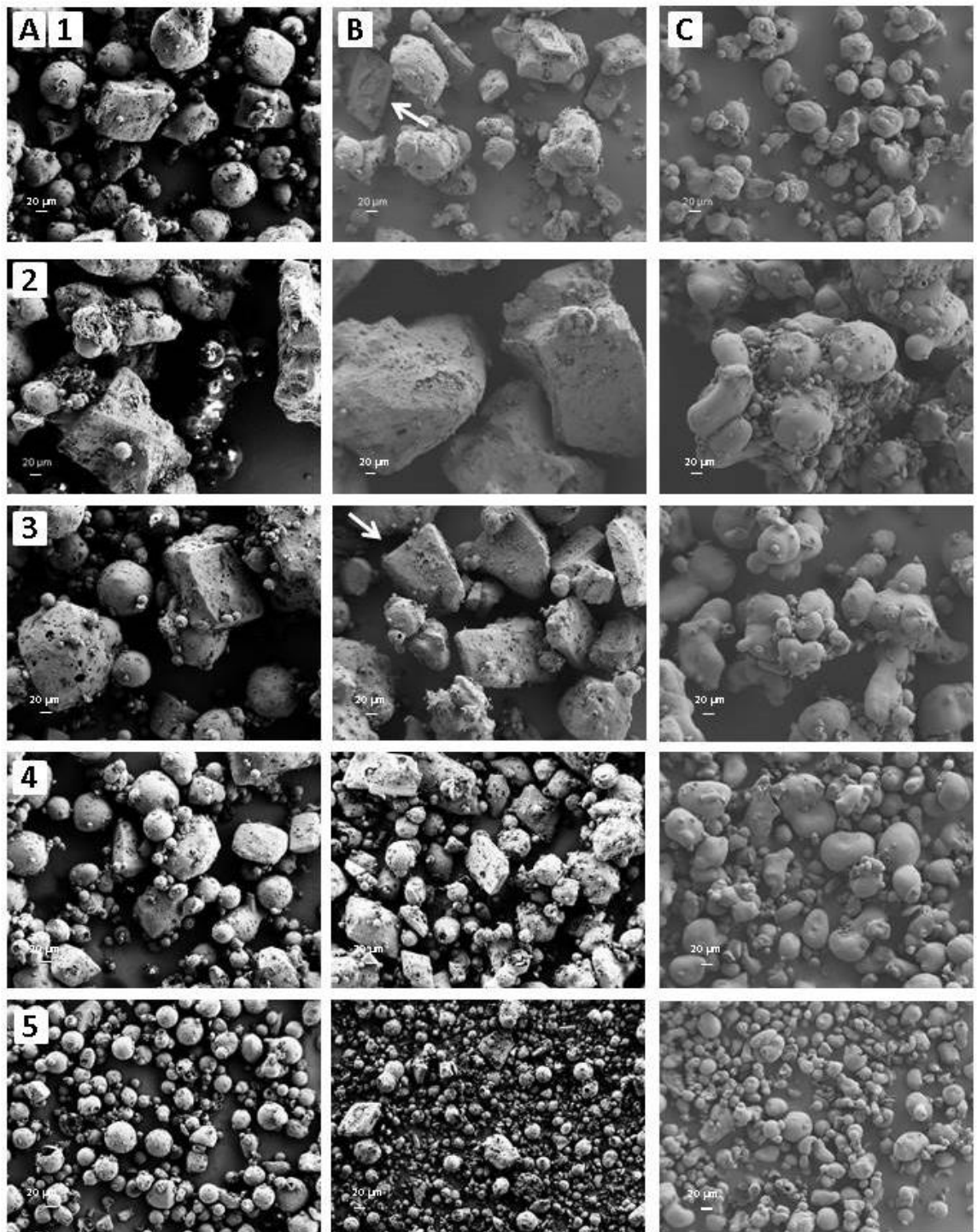
Particle size can affect surface composition due to differences in droplet drying times, allowing more or less migration of certain milk components to the particle surface. For example, Foerster et al. (2016) reported that protein migration to the particle surface was more prominent in droplets with larger diameters. The authors suggested that this may be due to the surface activity of the protein and differences in diffusivity between the various milk components. In keeping with those observations, Table 2.3 shows that there was a significant difference ( $P \leq 0.05$ ) in the amount of protein at the surface between the largest and the smallest size fraction of SMP ( $47.6 \pm 1.95\%$  and  $43.8 \pm 0.49\%$ , respectively). However, in a similar study investigating differences in surface composition of various size fractions of SMP, Kim et al. (2009) observed no significant effect of particle size on surface composition. It should be noted that the particle size range used in their study was very small (0-90  $\mu\text{m}$ ) and therefore the differences in size may not have been large enough to show any significant change in surface composition. For DWP and WPP, no clear influence of particle size on surface composition was observed (Table 2.3). However, disproportionately high levels of crude protein were observed at the surface of WPP powders in comparison to DWP, especially when considering the protein contents of

the bulk powders (Table 2.2). This may indicate a greater diffusivity of nitrogenous compounds in WPP particles during drying.

#### 2.3.1.3. Particle morphology

Scanning electron micrographs of the three original powders and their size fractions are shown in Fig. 2.1. For DWP and WPP, the semi-crystalline nature of the powders could be clearly seen, as they consisted of a mixture of sharp-edged lactose crystals and less regular/more globular amorphous powder particles. The non-crystalline particles in DWP appeared to be more spherical in shape compared to WPP. This may be due to the higher protein content of DWP, as protein formulation has been shown to influence particle morphology (Maa et al., 1997). The  $x < 75\ \mu\text{m}$  fraction of WPP also appeared to be comprised of smaller particles compared to the equivalent size fraction of DWP and SMP (Fig. 2.1, Sections 5A-C), which could have implications for the flowability of the powder (Fu et al., 2012). SEM images of SMP showed that the powder consisted mostly of agglomerated particles, and that the degree of agglomeration decreased with decreasing particle size.

The scanning electron micrographs from the two semi-crystalline powders also revealed differences in the types of lactose crystals present. In Fig. 2.1 (section B1) prism shaped crystals can be seen, whereas the crystals seen in Fig. 2.1 (section B3) had the characteristic tomahawk shape. Factors such as the level of supersaturation (Herrington, 1934; Parimaladevi and Srinivasan, 2014) and the impurities present (Garnier et al., 2002; Visser and Bennema, 1983) during crystallisation can affect the final lactose crystal shape. For example, Parimaladevi and Srinivasan (2014) showed that higher levels of supersaturation promoted the formation of prism shaped crystals, whereas Visser and Bennema (1983) concluded that tomahawk shaped crystals form as a result of the interference of  $\beta$ -lactose on the crystallisation process.



**Figure 2.1** Scanning electron micrographs of (A) demineralised whey powder (DWP), (B) whey permeate powder (WPP) and (C) skim milk powder (SMP) and their size fractions; (1) original, (2)  $x > 250 \mu\text{m}$ , (3)  $250 > x > 150 \mu\text{m}$ , (4)  $150 > x > 75 \mu\text{m}$  and (5)  $x < 75 \mu\text{m}$ , at 500 X magnification.

Another distinguishing feature from the SEM micrographs is the presence of small particulates on the surface of the lactose crystals in both of the semi-crystalline powders. This is likely due to the foam of the mother liquor adhering to the crystal surface during spray drying. Similar particulates were also observed by Kalab et al. (1991) in DWP, who describe them as 'lace-like ornamentations' on the surface of the lactose crystals.

#### 2.3.1.4. Glass transition temperature

Studies have shown that the  $T_g$  of a powder containing amorphous sugar is closely associated with the stickiness of that powder (Paterson et al., 2005), as the  $T_g$  signifies a decrease in surface viscosity and an increase in molecular mobility (Downton et al., 1982). The  $a_w$  of the original powders varied slightly at 0.34, 0.27 and 0.31 for the DWP, WPP and SMP, respectively (Table 2.4). For the three powders studied, the  $T_g$  midpoint of the original powders decreased as the amorphous lactose content of the powders increased; this is in keeping with other studies in which amorphous lactose content has been shown to have the greatest influence on  $T_g$  (Jouppila and Roos, 1994a, Shrestha et al., 2007).

**Table 2.4** Water activity ( $a_w$ ), glass transition temperature ( $T_g$ ), sticking point temperature (T) and difference between sticking point temperature and glass transition temperature ( $T-T_g$ ) for the original and fractionated demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP), before and after surface fat removal.<sup>a</sup>

	Size fraction	Water activity	$T_g$ (midpoint)	T	$T-T_g$	$T-T_g$ (after washing)
	( $\mu\text{m}$ )	( $a_w$ )	( $^{\circ}\text{C}$ )	( $^{\circ}\text{C}$ )	( $^{\circ}\text{C}$ )	( $^{\circ}\text{C}$ )
DWP	Original	0.34	$48.5 \pm 0.03^a$	68.1	19.6	n.d. <sup>d</sup>
	$x > 250$	0.36	$47.5 \pm 0.13^b$	67.7	20.2	n.d. <sup>d</sup>
	$250 > x > 150$	0.34	$48.8 \pm 0.01^a$	68.5	19.7	n.d. <sup>d</sup>
	$150 > x > 75$	0.35	$49.1 \pm 0.01^a$	42.9	-6.24	104
	$x < 75$	0.34	$48.6 \pm 0.48^a$	n.d. <sup>b</sup>	n.d. <sup>b</sup>	n.d. <sup>c</sup>
WPP	Original	0.27	$56.2 \pm 1.26^a$	70.9	14.7	n.d. <sup>d</sup>
	$x > 250$	0.36	$50.0 \pm 0.83^b$	58.2	8.20	n.d. <sup>d</sup>
	$250 > x > 150$	0.29	$53.7 \pm 0.05^c$	68.7	15.0	n.d. <sup>d</sup>
	$150 > x > 75$	0.28	$54.1 \pm 0.36^c$	62.5	8.35	n.d. <sup>d</sup>
	$x < 75$	0.28	$56.4 \pm 0.30^a$	n.d. <sup>b</sup>	n.d. <sup>b</sup>	n.d. <sup>d</sup>
SMP	Original	0.31	$37.7 \pm 0.08^a$	58.3	20.6	n.d. <sup>d</sup>
	$x > 250$		$33.4 \pm 0.21^b$	65.1	31.7	n.d. <sup>d</sup>
	$250 > x > 150$	0.30	$39.3 \pm 0.12^c$	60.6	21.3	n.d. <sup>d</sup>
	$150 > x > 75$	0.31	$39.3 \pm 0.93^c$	30.3	-9.00	27.8
	$x < 75$	0.31	$38.2 \pm 0.08^{ac}$	n.d. <sup>b</sup>	n.d. <sup>b</sup>	11.5
		0.31				

<sup>a</sup> For each powder, different superscript letters within the same column represent a significant difference ( $P \leq 0.05$ )

<sup>b</sup>  $T-T_g$  could not be calculated as stickiness could not be determined (n.d.).

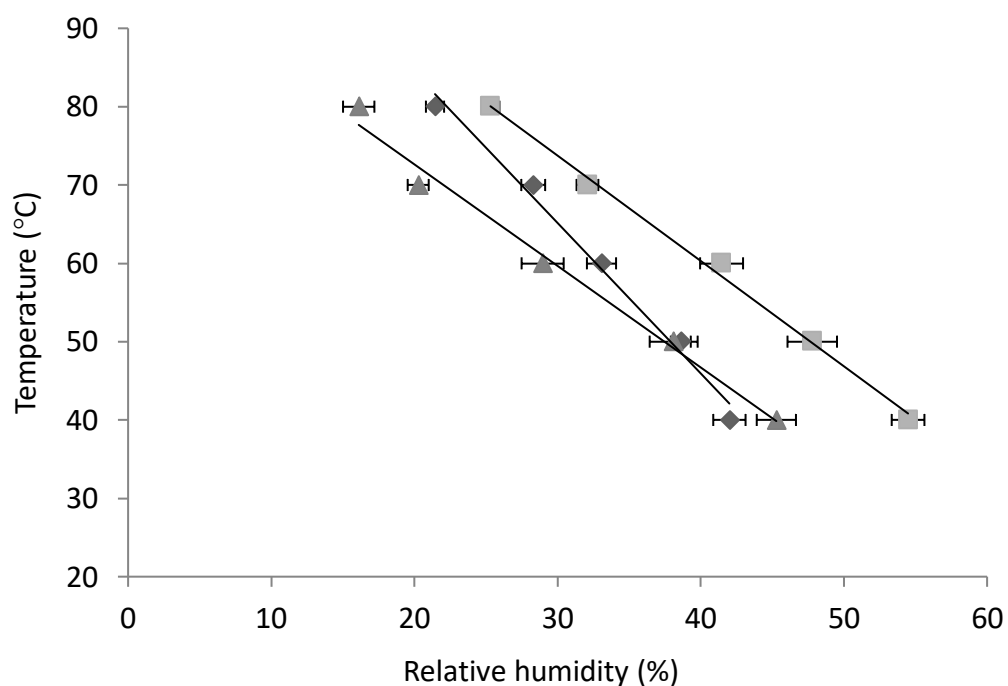
<sup>c</sup> Not enough powder remaining to wash surface

<sup>d</sup> Not analysed

### 2.3.2. Powder stickiness and hygroscopicity

#### 2.3.2.1. Stickiness of non-fractionated powders

Stickiness curves were generated for each powder by plotting the RH against the dry bulb temperature at which the powder became sticky. The areas above and below the curves represent the 'sticky' and 'non-sticky' zones respectively. Fig. 2.2 shows the stickiness curves for the original DWP, WPP and SMP. For all three powders examined, as the dry bulb temperature increased, the RH at which the powder became sticky decreased. The susceptibility of the powders to sticking increased in the order DWP < WPP < SMP, with SMP exhibiting sticky behaviour at the lowest temperature/RH conditions. Similar results were found by Hogan et al. (2009), who compared the stickiness of various dairy powders, including DWP and SMP.

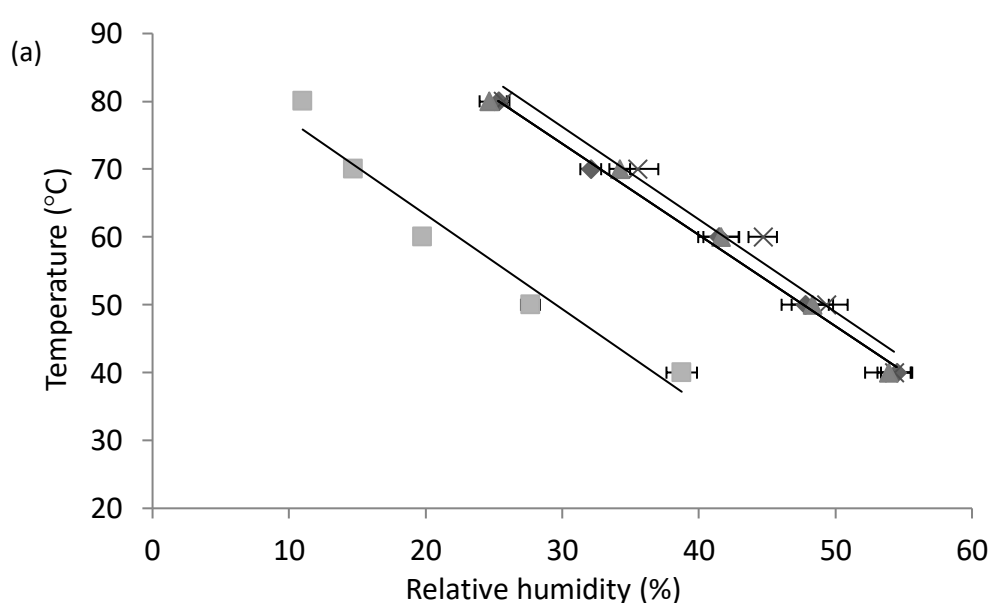


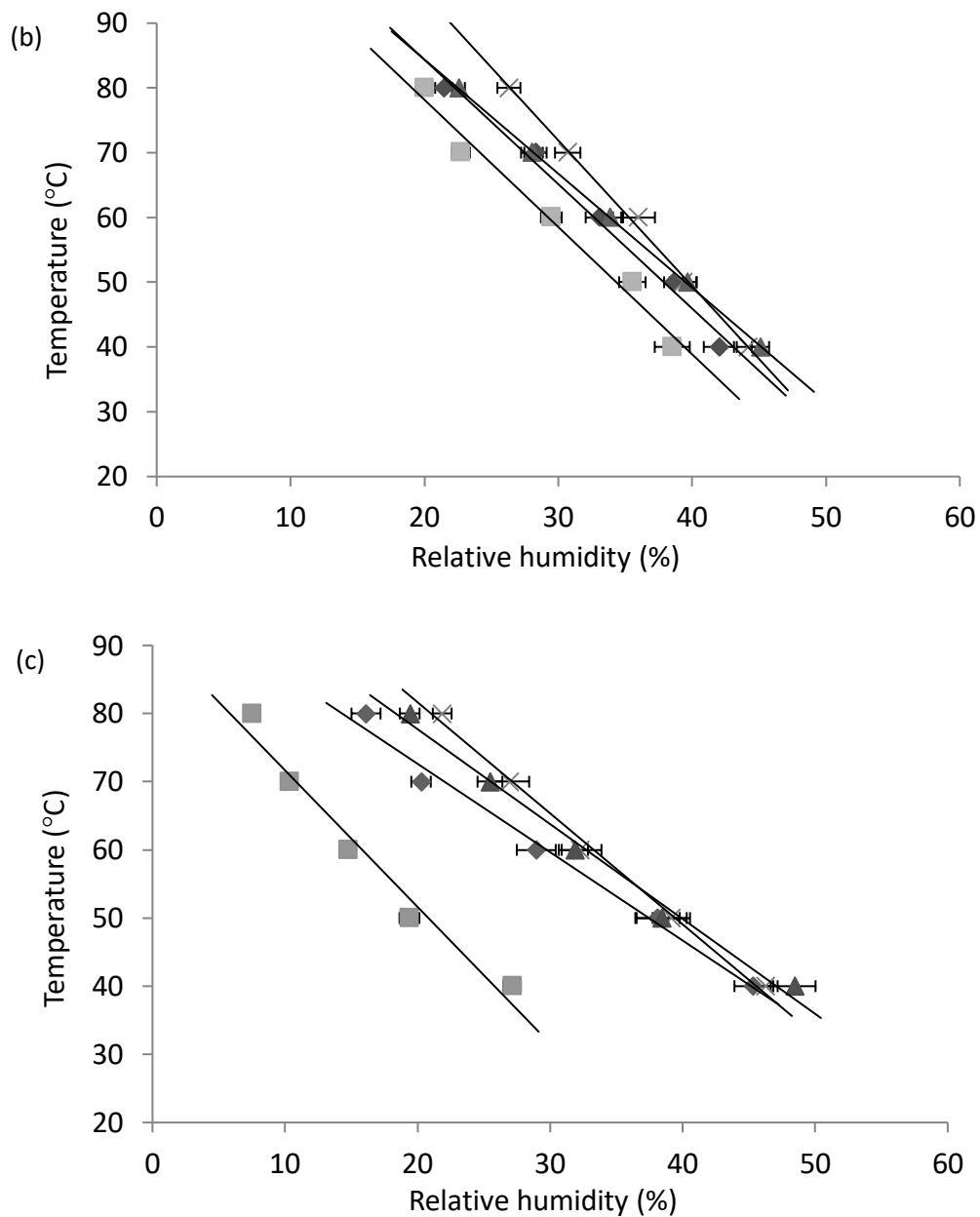
**Figure 2.2** Stickiness curves of the three original powders examined in the study; (■) demineralised whey powder (DWP), (◆) whey permeate powder (WPP) and (▲) skim milk powder (SMP).



Of the two semi-crystalline powders examined, WPP was found to be more susceptible to sticking than DWP, despite the fact that WPP had a higher  $T_g$  midpoint and would therefore be expected to have a higher sticking temperature. This may be explained by the higher protein content of DWP ( $11.4 \pm 0.28\%$ ) compared to WPP ( $3.52 \pm 0.05\%$ ); increasing the protein content of lactose-containing powders has been shown to significantly increase the  $T-T_g$ , and therefore protect against sticking (Hogan and O'Callaghan, 2010). This occurs due to the preferential sorption of water by the proteins, which reduces the amount of water available in the system and therefore reduces the rate of plasticisation of amorphous lactose (Hogan and O'Callaghan, 2010; Shrestha et al., 2007). This observation was supported by the  $T-T_g$  values obtained in this study for WPP and DWP (Table 2.4). In relation to surface composition, WPP was found to have a higher percentage of crude protein at the surface compared to DWP. However, this crude protein value is misleading as it is not possible to differentiate between true protein and NPN using XPS. Based on the bulk composition of the powders, it is probable that a greater proportion of the crude protein at the WPP surface is NPN, which may not have had the same retarding effect as higher molecular weight components on  $T_g$  and stickiness (Roos and Karel, 1991c).

#### 2.3.2.2. Influence of particle size on stickiness





**Figure 2.3** Stickiness curves showing the (◆) original, (X)  $x > 250 \mu\text{m}$ , (▲)  $250 > x > 150 \mu\text{m}$ , (■)  $150 > x > 75 \mu\text{m}$  fractions of the three powders examined; (a) demineralised whey powder (DWP), (b) whey permeate powder (WPP) and (c) skim milk powder (SMP).

Fig. 2.3 demonstrates the relationship between particle size and stickiness. Smaller particles were more susceptible to sticking in all three powders tested. Stickiness is thought to be influenced by particle size as smaller particles have a higher specific surface area (SSA), which promotes interaction and formation of liquid bridges with

one another and/or equipment surfaces. Likewise, inter-particle distance in a given volume will also be affected, resulting in an increase in collision frequency for smaller particles. Another explanation for the increased stickiness observed for the smaller fractions of the semi-crystalline powders could be due to a higher amorphous lactose content, compared to the larger fractions (Hogan and O'Callaghan, 2010, Hogan et al., 2009). However, these results do not agree with the findings by Hogan et al. (2009) who did not observe any effect of particle size on the stickiness of two SMP fractions with  $D[4,3]$  values of 130 and 61  $\mu\text{m}$ . The  $D[4,3]$  values of the  $250 > x > 150$  and  $150 > x > 75$   $\mu\text{m}$  fractions of SMP examined in this study were 124 and 83.2  $\mu\text{m}$ , respectively. A possible explanation for this disparity may be the use of a vibrating element in the apparatus used by Hogan et al. (2009), which may have served to disrupt inter-particle cohesion in the smaller size fractions. It should also be noted that the stickiness behaviour of the smallest fraction ( $x < 75$   $\mu\text{m}$ ) of each sample could not be determined due to excessive stickiness under ambient conditions (i.e., air channels developed instantly in the powder and no further fluidisation was observed).

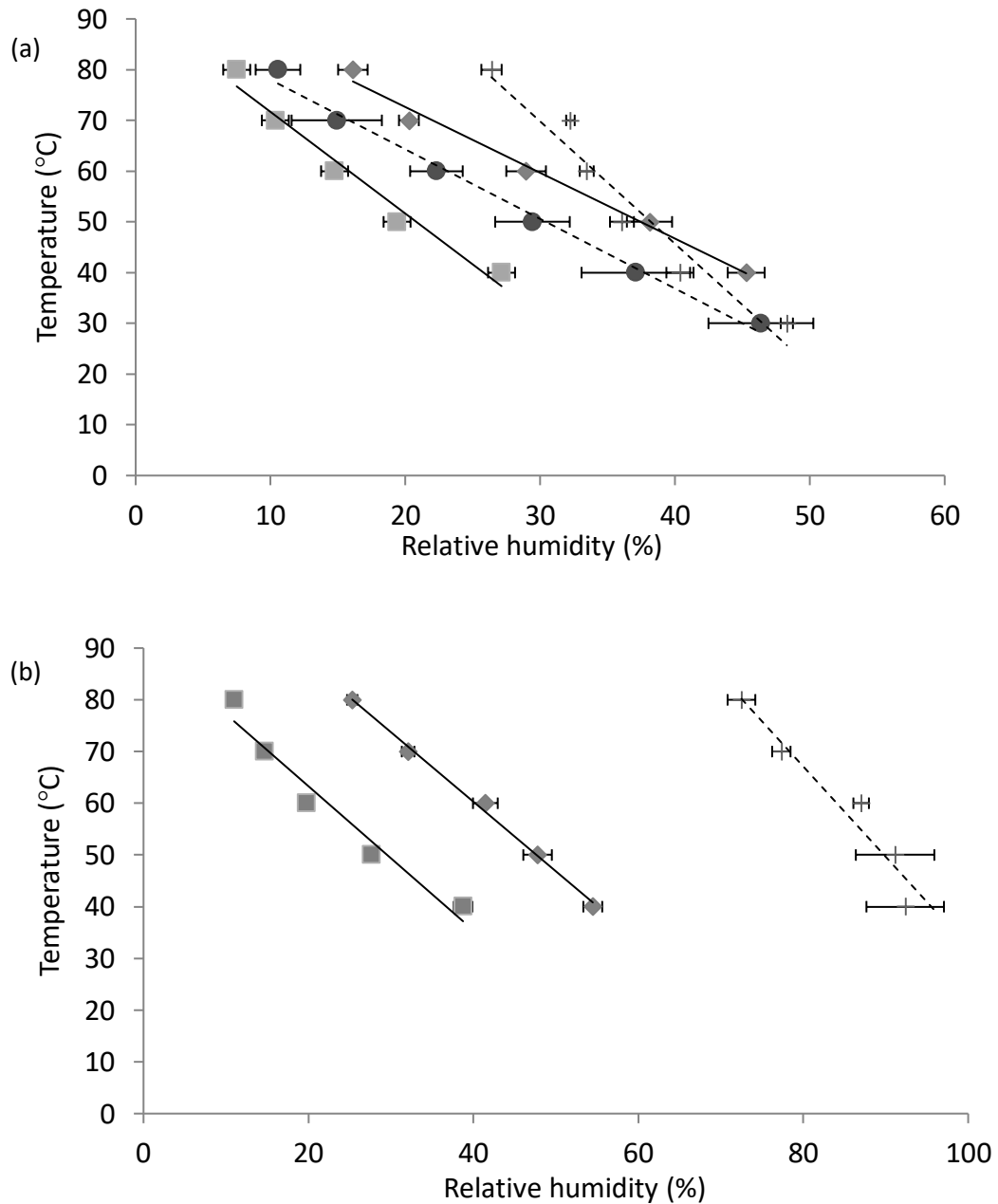
For both of the semi-crystalline powders there was no significant difference ( $P > 0.05$ ) in the amount of lactose present at the surface across the various size fractions (Table 2.3). However, as previously mentioned, the crystallinity of the lactose in the bulk of the semi-crystalline powders was found to be much higher in larger particles (Table 2.2). While it is not possible to measure the crystallinity of the lactose at the particle surface, these results may suggest that there could be a higher proportion of amorphous lactose at the surface of smaller particles, which would likely have contributed to their sticking behaviour (Murti, 2006). This may also explain the increased stickiness and lower  $T-T_g$  values (Table 2.4) observed for smaller size fractions of WPP and DWP. For SMP, slightly lower protein and higher lactose contents at the surface of the smaller particles may have accounted for increased stickiness; however, the surface compositional differences observed between fractions were not sufficient to explain the significant differences seen in Fig 2.3. For two of the size fractions (i.e., the  $150 > x > 75$   $\mu\text{m}$  fractions of the DWP and SMP) the

$T-T_g$  had a negative value (Table 2.4), indicating stickiness occurred prior to glass transition – an observation that contradicts many years of published literature. In light of these findings, further investigation was undertaken to determine if these observations were due to a) fluidisation issues or b) contribution of surface fat to stickiness.

In order to investigate whether the results obtained for the  $x < 75 \mu\text{m}$  fraction were due to poor fluidisation characteristics of the powder, the minimum air velocity required to fluidise each powder fraction was determined by measuring the pressure drop across an 80 mL fluid bed using a powder flow rheometer. For all size fractions tested, the minimum air velocity required to fluidise powders in the rheometer (data not shown) was lower than that passing through the fluid beds ( $0.12 \text{ m s}^{-1}$ ). These findings suggest that the poor fluidisation observed for the  $x < 75 \mu\text{m}$  samples in the stickiness apparatus was likely due to powder stickiness, which inhibited fluidisation due to cohesion between powder particles and/or adhesion of powder particles to the walls of the fluid bed.

Although the amorphous lactose content is considered the predominant cause of stickiness in dairy powders, fat present at the particle surface has also been shown to contribute (Özkan et al., 2002). In order to investigate the contribution of surface fat to particle stickiness, a petroleum ether wash was used to remove the surface fat from the  $150 < x < 75 \mu\text{m}$  fractions of all three powders and the  $x < 75 \mu\text{m}$  fraction of SMP. The stickiness behaviour of these fractions was then re-tested and the results are presented in Fig. 2.4. Both DWP and SMP showed significant improvements in stickiness behaviour for all size fractions after washing (i.e., higher temperature and RH conditions were required for the powders to become sticky). In particular, the  $150 < x < 75 \mu\text{m}$  fraction of DWP showed a very significant reduction in stickiness, which may be due to the higher amount of surface fat ( $26.2 \pm 3.51\%$ ) removed, compared to the equivalent SMP fraction ( $11.0 \pm 1.76\%$ ). The results for the  $x < 75 \mu\text{m}$  fraction of SMP are also particularly significant, as the stickiness of the previous sample containing surface fat could not be determined using the stickiness rig at all. It should

also be noted that the stickiness of WPP could not be re-tested due to extreme caking of the powder after washing.



**Figure 2.4** Stickiness curves showing the (♦) original, (■) 150 > x > 75 μm (before surface fat removal), (+) 150 > x > 75 μm (after surface fat removal) and (●) x < 75 μm (after surface fat removal) fractions of (a) skim milk powder (SMP) and (b) demineralised whey powder (DWP).

Particle size and lactose crystallinity of the three powder fractions were re-tested after washing in order to determine whether any other changes in physicochemical properties of the powders might have affected the stickiness results. The results showed that although there was no change in particle size, the lactose crystallinity of each powder did increase slightly, most likely as a result of exposure to atmospheric conditions during the evaporation of petroleum ether. The  $150 > x > 75 \mu\text{m}$  fraction of DWP had the greatest increase in crystallinity after washing, from 79.9 to 98.0%. The SMP fractions showed smaller increases in crystallinity, from 8.80 to 11.2% for the  $150 > x > 75 \mu\text{m}$  fraction and 3.66 to 4.05% for the  $x < 75 \mu\text{m}$  fraction. The larger increase in lactose crystallinity observed in DWP is likely to have contributed to the considerable improvement in the stickiness behaviour of this powder fraction after washing. Overall, it is difficult to determine the individual influence of the fat removal and the change in lactose crystallinity on the stickiness behaviour of these powder fractions, but considering the magnitude of the change in stickiness behaviour, it is likely a combination of both of these factors. Furthermore, if the surface fat is contributing to stickiness, this, in combination with a higher SSA (and contact between small particles), may help explain the increased stickiness observed in the original  $x < 75 \mu\text{m}$  fractions.

### 2.3.2.3. Hygroscopicity

Hygroscopicity of the powders is shown in Table 2.5. Of the three powders examined, SMP was the most hygroscopic ( $7.62 \pm 0.03$  at 43% RH), classifiable as a 'slightly hygroscopic powder' (Table 2.5). The values obtained for SMP at 43% RH, are predominantly due to the amorphous lactose content (46.9%) of the powder (Listiohadi et al., 2005), in combination with a relatively high protein content ( $36.4 \pm 0.56\%$ ). The two semi-crystalline powders absorbed less moisture than SMP due to their higher crystalline lactose content (Bronlund and Paterson, 2004). Of these, WPP was more hygroscopic ( $3.74 \pm 0.02$  at 43% RH) than DWP ( $2.17 \pm 0.00$  at 43% RH), which may be due to its higher mineral content (Ibach and Kind, 2007; Shrestha et al., 2008).

**Table 2.5** Hygroscopicity of the original and fractionated demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP) at 43% relative humidity (RH). Classification of powder hygroscopicity at 43% relative humidity (RH) was modified from Schuck et al. (2012).<sup>a</sup>

	Size fraction ( $\mu\text{m}$ )	Hygroscopicity at 43% RH	Classification at 43% RH <sup>b</sup>
DWP	Original	$2.71 \pm 0.00^a$	Non-hygroscopic
	$x > 250$	$2.00 \pm 0.00^b$	Non-hygroscopic
	$250 > x > 150$	$2.61 \pm 0.07^c$	Non-hygroscopic
	$150 > x > 75$	$2.94 \pm 0.02^d$	Non-hygroscopic
	$x < 75$	$5.00 \pm 0.00^e$	Slightly hygroscopic
WPP	Original	$3.74 \pm 0.02^a$	Non-hygroscopic
	$x > 250$	$0.78 \pm 0.01^b$	Non-hygroscopic
	$250 > x > 150$	$3.22 \pm 0.05^c$	Non-hygroscopic
	$150 > x > 75$	$4.23 \pm 0.02^d$	Non-hygroscopic
	$x < 75$	$7.20 \pm 0.03^e$	Slightly hygroscopic
SMP	Original	$7.62 \pm 0.03^a$	Slightly hygroscopic
	$x > 250$	$7.61 \pm 0.02^a$	Slightly hygroscopic
	$250 > x > 150$	$7.78 \pm 0.01^b$	Slightly hygroscopic
	$150 > x > 75$	$7.60 \pm 0.01^a$	Slightly hygroscopic
	$x < 75$	$7.68 \pm 0.03^c$	Slightly hygroscopic

<sup>a</sup> For each powder, different letters within the same column represent a significant difference ( $P \leq 0.05$ ).

<sup>b</sup> Note: Non-hygroscopic powder:  $\leq 4.5$ ; Slightly hygroscopic powder: 4.6-8.0; Hygroscopic powder: 8.1-11.0; Very hygroscopic powder: 11.1-14.5; Extremely hygroscopic powder:  $\geq 14.5$

Particle size can also affect the hygroscopicity of a powder as moisture uptake occurs primarily on the particle surface. As such, smaller particle sizes have a relatively larger exchange surface for water absorption to occur, and vice versa. In the current study, powder hygroscopicity increased linearly with decreasing particle size for both DWP

and WPP (Table 2.5). Carpin et al. (2017a) observed similar water uptake in smaller size fractions of crystalline lactose powders. This water absorption is likely due to the increased amount of hygroscopic components, such as amorphous lactose, proteins and minerals, present in smaller fractions. However, the same pattern was not observed for the SMP sample, which showed very little variation in hygroscopicity across all size fractions ( $7.60 \pm 0.01 - 7.78 \pm 0.01$  at 43% RH). These results suggest that the influence of particle size on powder hygroscopicity appears minimal, and that differences in hygroscopicity observed between size fractions of the same powder may be primarily due to differences in composition.

## 2.4 Conclusions

The results presented show that significant differences in composition, stickiness behaviour and hygroscopicity exist between the various size fractions of SMP, WPP and DWP. There was a clear distinction observed between powders – DWP and WPP were semi-crystalline powders consisting of mixtures of crystalline lactose and non-crystalline particles, while SMP was composed of largely agglomerated, non-crystalline particles. This distinction was a key determinant in both the fractionation and physicochemical behaviours of resultant powders.

Bulk composition of semi-crystalline powder fractions (DWP and WPP) was greatly affected by particle size; large size fractions were more crystalline compared to smaller fractions, which also had higher protein contents. Smaller size fractions exhibited greater tendency towards stickiness and hygroscopicity, leading to the conclusion that differences in bulk composition were the most significant contributory factor to the differences in physicochemical behaviour. In contrast, bulk composition did not vary across SMP size fractions.

Hygroscopicity of all SMP size fractions was relatively constant, again suggesting that bulk composition was the major determinant for water absorption, rather than particle size. Stickiness behaviour of all three powders, however, was closely related



to size, with smaller size fractions exhibiting higher stickiness. It was suggested that this was due to a combination of increased particle surface area and fat coverage.

Overall, this study shows that significant differences exist in stickiness and hygroscopic properties of dairy powders as a function of both composition and particle size. The increased susceptibility of fine particles to stickiness/hygroscopicity is particularly interesting and should be better incorporated into spray drying operational procedures.

### **Chapter 3: Comparison of differential scanning calorimetry and dynamic mechanical analysis with a fluidisation method for stickiness determination of whey protein powders**

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**Abstract**

There are a wide variety of methods currently available to characterise the stickiness behaviour of dairy powders, such as those that directly measure changes in particle cohesion/adhesion when subjected to higher temperatures and humidities, or the indirect approaches that track changes in a specific property of the material, such as the heat capacity or viscoelasticity. In the current study, the mechanical  $\alpha$ -relaxation results for a selection of model whey protein concentrate (WPC) powders with varying protein contents were compared to methods for stickiness and glass transition determination. The  $\alpha$ -relaxation temperatures ( $T_a$ ) were derived from both the storage and loss moduli using dynamic mechanical analysis (DMA). The glass transition temperatures ( $T_g$ ) of the WPC powders were determined using differential scanning calorimetry (DSC), and the stickiness behaviour was characterised using a fluidisation technique. For the lower protein powders (~19.3% and 35.7% protein w/w), the mechanical  $\alpha$ -relaxation temperatures, determined from the storage modulus of the DMA ( $T_a$  onset), were in good agreement with the fluidisation results, whereas for higher protein powders (~53.4 and 69.1% protein w/w), the fluidisation results compared better to the results determined from the loss moduli of the DMA ( $T_a$  peak). The temperature difference between the sticking temperature and glass transition temperature ( $T-T_g$ ) was found to be dependent on the point on the curves from which the  $T-T_g$  was determined, as well as the measuring technique used. This study demonstrates that DMA is a useful technique to complement stickiness characterisation of dairy powders. In particular, the data generated by DMA in relation to storage and loss modulus changes show promise as a means of attaining increased understanding of the mechanism of stickiness.

### 3.1 Introduction

Stickiness of powders is a major challenge encountered by dairy processors, especially during the spray drying of products with high lactose contents, as it leads to lower powder yields and inferior powder quality. Stickiness in lactose-containing powders occurs predominantly due to the glass transition phenomenon, in which a phase change occurs in the amorphous material on exposure to high temperature and/or relative humidity (RH) conditions. This lowers the viscosity of the powder particle surface, allowing liquid bridges to form between particles, resulting in cohesion between particles and/or adhesion to equipment surfaces. A considerable amount of work has been performed developing stickiness characterisation techniques that can estimate the temperature and RH conditions at which individual dairy powders will become sticky (Boonyai et al., 2002; Chuy and Labuza, 1994; Hogan et al., 2009; Özkan et al., 2002; Paterson et al., 2001; Silalai and Roos, 2011b; Zuo et al., 2007,). This information has become useful to dairy processors at helping to minimise challenges during spray drying, allowing for the alteration of drying parameters to ensure that temperature and RH conditions within dryers are such that powder stickiness is avoided. Furthermore, these methods are also beneficial to dairy scientists to allow them to gain a deeper understanding of the wide variety of factors affecting the stickiness behaviour of dairy powders.

There are a wide variety of methods available to determine the stickiness behaviour of dairy powders, which can be classified as either direct or indirect techniques. Direct methods are perhaps the most accurate, as they measure the changes in a property of the powder, such as the viscosity or resistance to shear. One of the original direct stickiness measurement techniques is a propeller-driven device first created by Lazar et al. (1956) for use on tomato powder, in which the force required to move a stirrer in a bed of powder was measured. This method was later modified and used for stickiness characterisation of dairy powders by Chuy and Labuza (1994), Hennigs et al. (2001) and Özkan et al. (2002). However, as this method is performed under static conditions, the results are likely to be more representative of the interactions that occur during storage of powders, due to the increased inter-particle

surface contact (Hogan et al., 2009). In contrast, pneumatic methods, in which the particles come into direct contact with an air stream of increasing/alternating RH, may be considered to be more accurate, as they most closely simulate the conditions that occur during spray drying. Examples of pneumatic methods that have been used to characterise the stickiness behaviour of dairy powders include; the fluidisation rigs used by Hogan et al. (2009) and Murti et al. (2010), the blow test method developed by Brooks (2000) and Paterson et al. (2001), the cyclone stickiness test first reported by Boonyai et al. (2002), and the particle gun created by Zuo et al. (2007). However, the stickiness curves generated from these methods can also differ due to differences in air velocities (Murti et al., 2010), particle trajectories and contact times between particles and the air stream.

One indirect approach that has been well established and commonly used to estimate stickiness development in dairy powders is the determination of glass transition temperature ( $T_g$ ). The  $T_g$  can be defined as the temperature at which the glass transition takes place, and is normally determined either by measurement or estimation using mathematical modelling, such as the Couchman-Karasz equation (Couchman and Karasz, 1978); the measurement approach is considered more precise, as it allows tracking of changes that occur in a specific property of the material during the phase change. For example, differential scanning calorimetry (DSC) measures the changes that occur in specific heat capacity of the sample during the glass transition, and has been widely used to determine the  $T_g$  of dairy powders (Chuy and Labuza, 1994; Haque and Roos, 2004a; Haque and Roos, 2004b; Jouppila and Roos, 1994a; Maidannyk and Roos, 2017; O'Donoghue et al., 2019; Ozmen and Langrish, 2002; Silalai and Roos, 2010; Silalai and Roos, 2011b). It should be noted that while the glass transition determination is not a stickiness test method, a relationship does exist between the  $T_g$  and sticking point temperature (SPT), which can be used to roughly estimate the sticking temperature. One of the first studies to compare the  $T_g$  to the SPT, which was determined using the method by Lazar et al. (1956), reported that the SPT was approximately 10-15°C higher than the  $T_g$  onset (Roos and Karel, 1991b). However, the extent to which the temperature must exceed

the  $T_g$  in order for sticking to occur is not consistent, even for the same powder, as it depends on a wide variety of factors, such as the powder composition (Hogan et al., 2009), exposure time (Karel et al., 1994) and the methods used to determine both the SPT and  $T_g$  (Boonyai et al., 2004). This is evident in the range of  $T-T_g$  values that have been reported for skim milk powder (SMP); 20.6°C (O'Donoghue et al., 2019), 29°C (Hogan et al., 2009), 33.6°C (Murti et al., 2009), 14-22°C (Ozmen and Langrish, 2002) and 23.3°C (Hennigs et al., 2001). The determination of  $T_g$  alone is therefore not an accurate method for stickiness characterisation, as although there is a correlation between the SPT and  $T_g$ , it is difficult to predict the precise temperature above the  $T_g$  that sticking will occur (Boonyai et al., 2004). Hence, further research is required in order to develop an empirical relationship for predicating SPT, using  $T_g$ .

Another indirect method that has recently been related to the stickiness phenomenon is dynamic mechanical analysis (DMA), also referred to as dynamic mechanical thermal analysis (DMTA), which has been used in many studies to determine mechanical  $\alpha$ -relaxations of amorphous food materials (Fan and Roos, 2016; Fan and Roos, 2017; Silalai and Roos, 2011a; Silalai and Roos, 2011b). Mechanical  $\alpha$ -relaxations describe the changes in the physical state of the material around the glass transition and could therefore also be good indications of the changes in viscosity that occur during stickiness development. Furthermore, as DMA is a highly sensitive method, it may provide an opportunity to develop a greater understanding of the mechanisms of stickiness development (i.e., changes in viscoelastic behaviour) when the results are compared to other binary (i.e., sticky/non-sticky) methods. The DMA method involves subjecting the sample to a sinusoidal force and measuring the amount of energy stored (storage modulus) and lost (loss modulus) from the sample. During the glass transition, as the material 'relaxes' from an amorphous into a crystalline state, there will be a sudden decrease in the storage modulus ( $E'$ ) and a corresponding increase in the loss modulus ( $E''$ ). Silalai and Roos (2011b) compared the results obtained from DMA to a sticky point tester, modified from the design by Lazar et al. (1956), and found that the  $\alpha$ -relaxation temperatures (calculated from the peak of the loss modulus) were good

indicators for stickiness development for SMP/maltodextrin mixes. However, the sticky point tester used in that study is a viscometry-based technique, which may not produce the most accurate stickiness characterisation results compared to pneumatic techniques. Furthermore, the SMP/maltodextrin powders examined in this study are also not representative of the wide range of dairy powders currently on the market. For example, the primary carbohydrate in the majority of the powders was maltodextrin (rather than lactose) and the highest protein content powder examined in that study was that of the original SMP (~35% w/w).

The objective of the current study is to compare the  $\alpha$ -relaxation temperatures ( $T_a$ ) derived from the storage and loss moduli using DMA to methods commonly used to measure phase transitions (DSC) and stickiness behaviour (fluidisation) for a selection of whey protein concentrate (WPC) powders. When compared to the fluidisation method, DMA may also provide an opportunity to gain a greater understanding of the mechanical changes occurring during stickiness development.

## **3.2 Materials and methods**

### **3.2.1 Materials**

Whey protein concentrate (WPC) 80 powder and whey permeate powder (WPP) were supplied by local dairy companies. Model WPC powders were produced for this purpose of this study by mixing the WPC 80 and WPP and reconstituting with water at different proportions to produce WPCs with target protein contents of 20, 35, 50 and 65% (w/w). These WPC80/permeate solutions were then spray dried using an Anhydro three-stage drier with fines return to the top of the drier (SPX Flow Technology, Soeborg, Denmark), using a two-fluid nozzle atomiser. Solid contents of the concentrates were 42, 40, 36 and 32% for the WPC 20, 35, 50 and 65, respectively. All powders were dried using inlet and outlet temperatures of 180 and 80°C, respectively, and the final stage of drying was completed in an external fluid bed at 60°C. The WPC powders were then stored in foil bags at 16°C prior to analysis. All analysis was carried out within 6 months of manufacture.

### 3.2.2 Powder composition

Protein content was determined using a LECO Nitrogen Analyser FP-638 (LECO Corporation, Michigan, USA), using a nitrogen-to-protein conversion factor of 6.38. Fat content was determined by Röse-Gottlieb (IDF, 1987). Ash content was analysed after overnight incineration in a muffle furnace at 550°C. Free moisture was determined after drying in an oven at 86°C for 6 h. Lactose content was calculated by difference. Particle size was measured by laser light scattering using a Mastersizer 3000 (Malvern Instruments Ltd., UK), equipped with an Aero S dry powder dispersion unit.

### 3.2.3 Stickiness by fluidisation

In the current study, a fluidisation technique, previously described by Hogan et al. (2009), was used to determine the sticking point temperature (SPT) ( $T_f$ ) of each powder. Stickiness curves were generated for each sample by plotting the air (dry bulb) temperature against the relative humidity (RH) (calculated from the saturated air temperature and absolute humidity) at which fluidisation ceased.

### 3.2.4 Powder equilibration

Powder samples (2 g) were transferred into glass vials and dried overnight in a vacuum oven (Jeio Tech 665L Vacuum Oven OV-12, Fisher Scientific, Leicestershire, UK) at 45°C. The dried samples were equilibrated in evacuated desiccators over saturated salt solutions of LiCl, CH<sub>3</sub>COOK, MgCl<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub> (Sigma Chemical Co., St. Louis, Mo., USA), with corresponding relative water vapour pressures (RVPs) of 11.4, 23.1, 33.2 and 44.1%, respectively, at room temperature (23–24°C) for 14 d.

### 3.2.5 Differential scanning calorimetry

A differential scanning calorimeter (DSC Q2000; TA Instruments, Crawley, UK) was used to determine the glass transition temperatures ( $T_g$ ) of the equilibrated powders, as described by Murphy et al. (2015). Hermetically sealed DSC aluminium pans, containing ~16 mg of powder, were heated in a nitrogen purged environment using



an empty aluminium pan as a reference. The samples were subjected to the following thermal profile; heating from approximately 40°C below to 40°C above the  $T_g$  at 5°C min<sup>-1</sup>, cooling back to 50°C below the  $T_g$  at 10°C min<sup>-1</sup>, and finally heating at 5°C min<sup>-1</sup> to an end temperature of 50°C above the  $T_g$ . The  $T_g$  onset values were determined from the second heating cycle using the TA Universal Analysis software. All analyses were completed in duplicate.  $T-T_g$  values were calculated by extracting the equation of the lines for the stickiness and glass transition curves and subtracting the y values at a given RH (x value).

### 3.2.6 Dynamic mechanical analysis

A dynamic mechanical analyser (DMA Q800, TA Instruments, New Castle, UK) with 35 mm dual cantilever clamp was used to determine the  $\alpha$ -relaxation temperature ( $T_a$ ) of the equilibrated powders. Approximately 400 mg of equilibrated powder was loaded into a stainless steel powder sample tray and the surface of the powder bed was levelled off and covered with a stainless steel lid. The powder sample tray and lid were then inserted into the clamp and tightened using a screw driver with a set torque (level 8). The analyses were carried out dynamically at a heating rate of 2°C/min, from approximately 50°C below the onset temperature of the decrease in storage modulus to 50°C above the onset temperature at frequencies of 1.0, 5.0, 10.0, and 20.0 Hz. However, it was found that there was no significant difference in the temperature at which the storage modulus decreased at frequencies greater than 10.0 Hz. Therefore, all the  $T_a$  values were determined at 10 Hz.  $T_a$  was determined from the onset in the decrease in the storage modulus ( $T_a$  onset), and the peak of the loss modulus ( $T_a$  peak), using the TA Universal Analysis software. A liquid nitrogen tank (50 L; CFL-50, Cryofab Inc, Kenilworth, USA) was connected to the dynamic mechanical analyser for cooling below room temperature. The  $T_a$  of each powder with various RVPs was measured in duplicate. Prior to sample analysis, the dynamic mechanical analyser was regularly calibrated using a stainless steel bar.

### 3.3 Results

#### 3.3.1 Relationship between powder composition and glass transition temperature

The composition and particle size of each powder is reported in Table 3.1. Protein contents for the WPC 20, 35, 50 and 65 were 19.3, 35.7, 53.4 and 69.1 (% w/w), respectively. Particle size has been shown to affect the stickiness behaviour of dairy powders (O'Donoghue et al., 2019); however, in the present study, there was very little difference in particle size between the four powders (D[4,3] values of 106 – 118  $\mu\text{m}$ ), therefore it is unlikely to be a contributing factor in their stickiness behaviour.

The  $T_g$  onset of the WPC powders are reported in Table 3.2. As expected, all four powders showed a decrease in  $T_g$  onset with increasing water activity ( $a_w$ ) (Haque and Roos, 2004a; Jouppila and Roos, 1994a; Ozmen and Langrish, 2002; Shrestha et al., 2007; Silalai and Roos, 2010,). This is due to the plasticising effect of water on the amorphous material, which increased the molecular mobility of the system,

**Table 3.1** Composition of whey protein concentrate (WPC) powders with protein contents ranging from ~20 (WPC 20) to ~65% (WPC 65).

Sample	Protein (% w/w)	Fat (% w/w)	Lactose <sup>a</sup> (% w/w)	Ash (% w/w)	Free moisture (% w/w)	Particle size D[4,3] <sup>b</sup> ( $\mu\text{m}$ )
WPC 20	19.3 $\pm$ 0.02	1.31 $\pm$ 0.04	66.2	7.34 $\pm$ 0.01	5.90 $\pm$ 0.01	106
WPC 35	35.7 $\pm$ 0.20	3.19 $\pm$ 0.06	48.6	6.36 $\pm$ 0.00	6.11 $\pm$ 0.08	118
WPC 50	53.4 $\pm$ 0.15	4.15 $\pm$ 0.02	32.8	5.59 $\pm$ 0.24	4.07 $\pm$ 0.14	118
WPC 65	69.1 $\pm$ 0.38	5.33 $\pm$ 0.03	17.5	4.23 $\pm$ 0.00	3.90 $\pm$ 0.05	115

<sup>a</sup> Calculated by difference

<sup>b</sup> D[4,3] = volume mean diameter

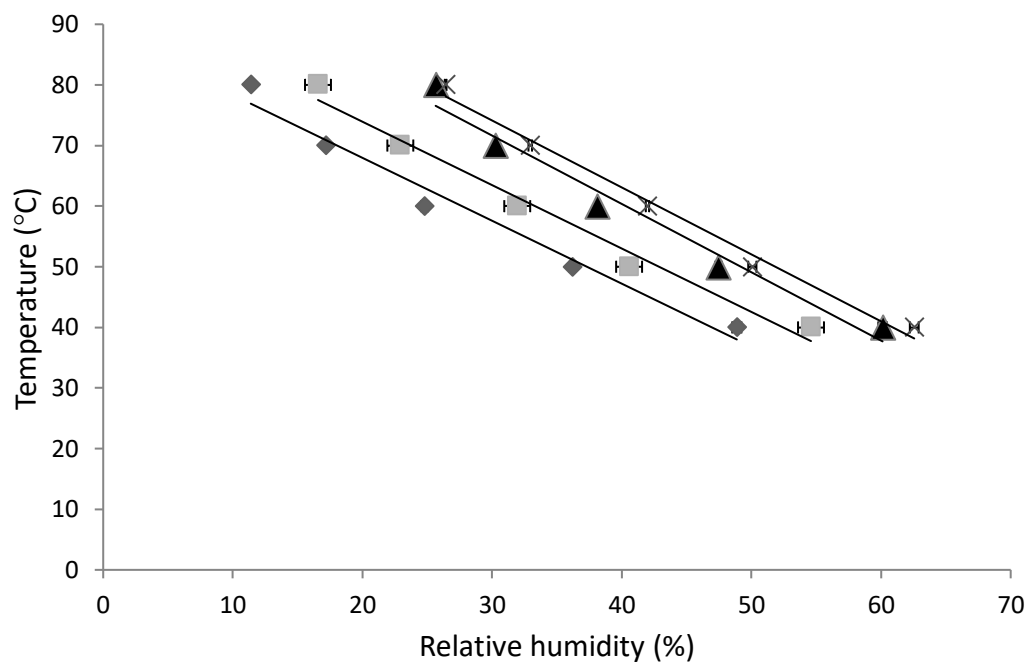
resulting in a decrease in  $T_g$  (Roos and Karel, 1991a). Studies have shown that the amorphous lactose content is the main determinant of the  $T_g$  in dairy powders (Shrestha et al., 2007; Silalai and Roos, 2010). In the current study, the  $T_g$  onset was also found to decrease with increasing lactose content. This trend was more pronounced in samples with  $a_w \geq 0.33$ . This may be due to the increased moisture availability in higher  $a_w$  samples, resulting in increased water plasticisation of the amorphous lactose.

### 3.3.2 Powder fluidisation analysis

Stickiness curves for each powder were generated using the fluidisation approach by plotting the dry bulb temperature against the RH at which sticking occurred (Fig. 3.1). The area above the stickiness curve represents the temperature and RH conditions where problems with stickiness are likely to occur, whereas the area below the curve represents the conditions considered safe during spray drying. For all four powders examined, as the dry bulb temperature increased, the RH at which the powder became sticky decreased. The susceptibility of the powders to sticking decreased in the order WPC 20 > WPC 35 > WPC 50 > WPC 65, with WPC 65 demonstrating the least sticky behaviour. This was expected, as the stickiness of

**Table 3.2** Onset temperatures for glass transition ( $T_g$ ) of whey protein concentrate (WPC) powders with protein contents ranging from ~20 (WPC 20) to ~65% (WPC 65), stored at different water activities ( $a_w$ ).

Sample	0.11 $a_w$	0.23 $a_w$	0.33 $a_w$	0.44 $a_w$
WPC 20	63.2 ± 0.56	50.6 ± 0.00	37.1 ± 0.25	18.6 ± 0.07
WPC 35	62.2 ± 0.01	49.9 ± 0.17	40.9 ± 0.60	21.6 ± 0.01
WPC 50	64.4 ± 0.13	47.6 ± 0.30	44.8 ± 0.26	33.7 ± 0.42
WPC 65	67.8 ± 0.23	52.4 ± 0.10	47.3 ± 0.23	42.7 ± 0.03

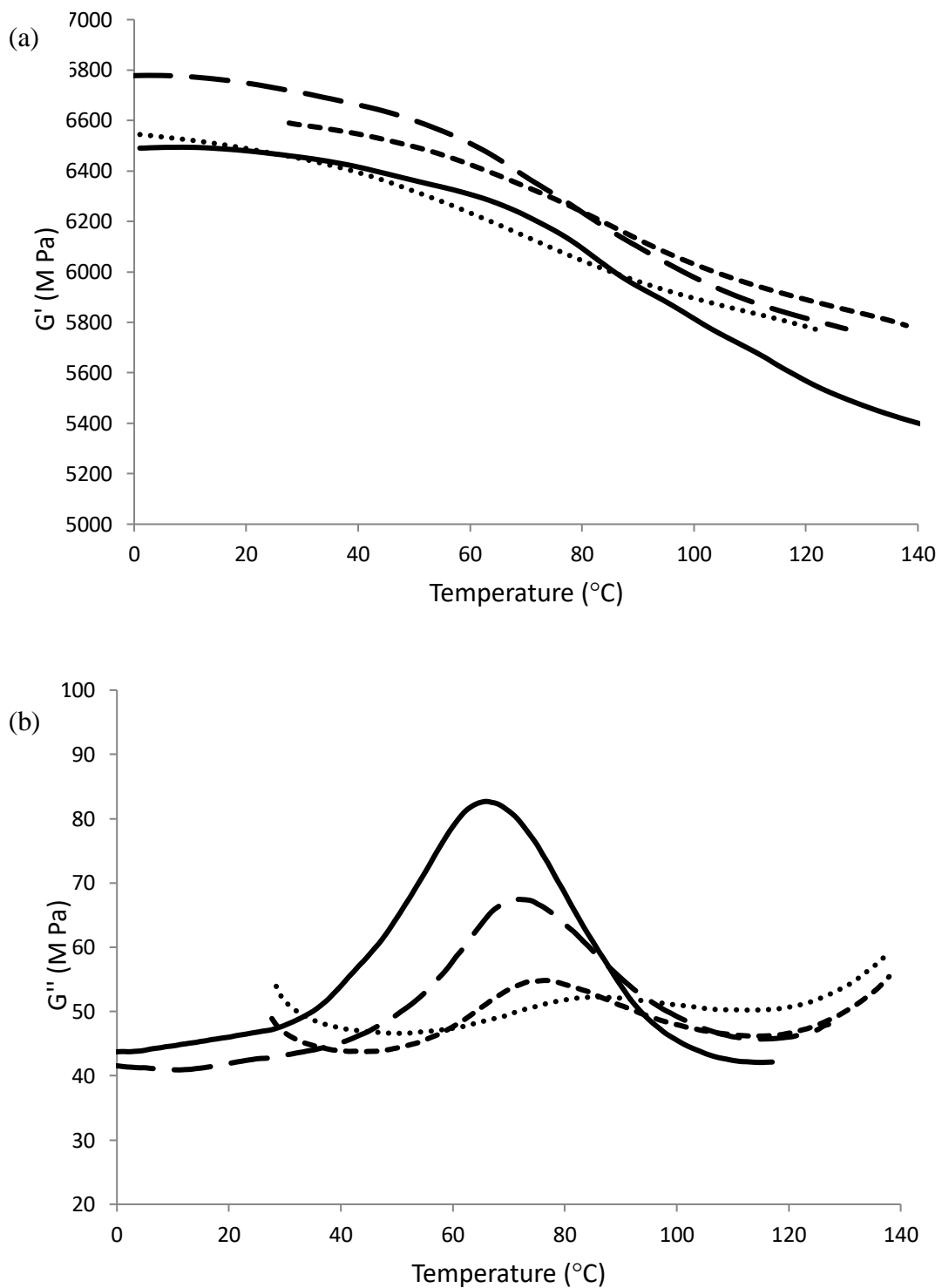


**Figure 3.1** Stickiness curves for whey protein concentrate (WPC) powders; (◆) WPC 20, (■) WPC 35, (▲) WPC 50 and (×) WPC 65, determined using the fluidisation technique.

dairy powders has been shown to decrease with increasing protein content (Hogan and O’Callaghan, 2010; Silalai and Roos, 2010). There is limited information available on the stickiness characterisation of WPC powders; however, the SPT results obtained for the WPC 35 powder are similar to those reported by O’Donoghue et al. (2019), for SMP using the same fluidisation method.

### 3.3.3 Dynamic mechanical analysis

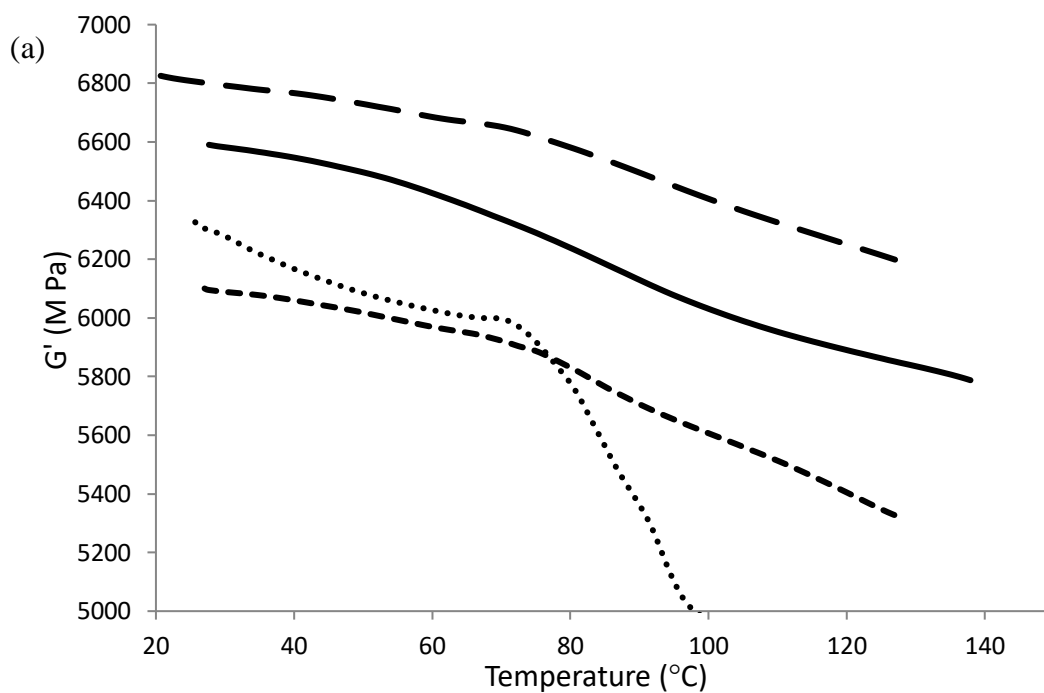
Fig. 3.2 shows the mechanical  $\alpha$ -relaxations for the WPC 65 over a range of  $a_w$  (0.11-0.44). As expected, significant changes occurred in the molecular mobility of the powder with increasing temperature. The magnitude of these changes, especially for the loss moduli (Fig. 3.2, b), were found to increase with increasing  $a_w$ , and this general trend was evident in all powders examined. The increased magnitude of the changes with increasing  $a_w$  is a result of the plasticizing effect of water, which increases the molecular mobility of the system (Silalai and Roos, 2011b). This causes a decrease in the viscosity of the particle surface, leading to the onset of sticking (Downton et al., 1982).

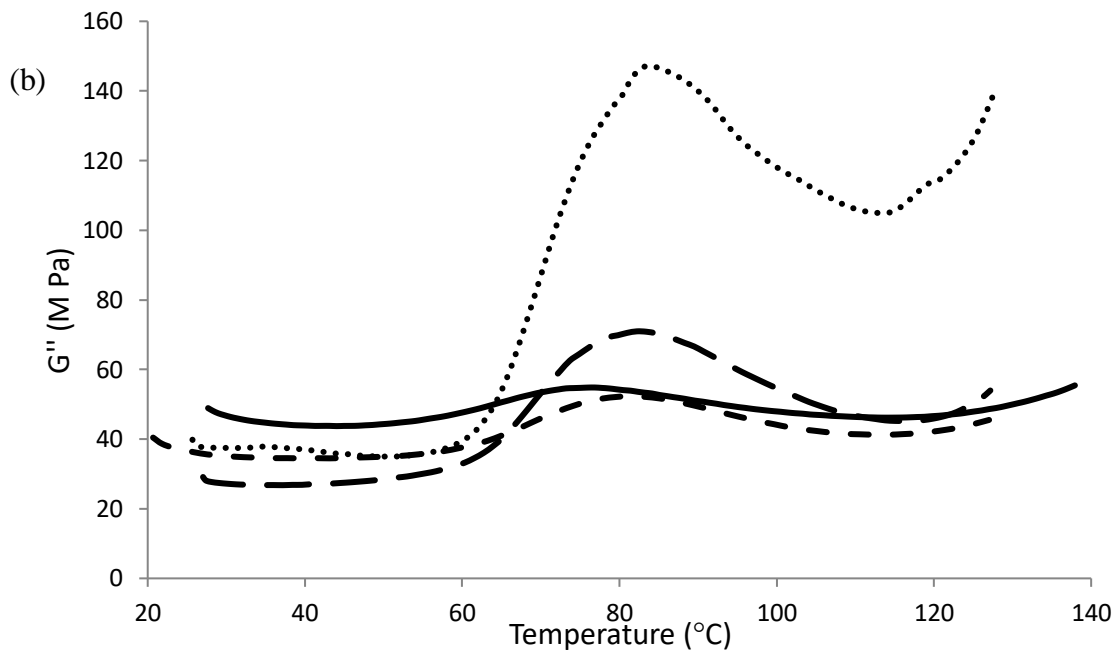


**Figure 3.2** Storage (a) and loss (b) moduli of whey protein concentrate (WPC) 65 powder at selected water activities ( $a_w$ ) of 0.11 (···), 0.23 (---), 0.33 (— —), and 0.44 (—).

In the current study, the magnitude of the changes in the  $\alpha$ -relaxations was also found to be dependent on powder composition (Fig 3.3). The higher the protein

content of the powder, the smaller the magnitude of the change in the moduli (Fig 3.3). Many studies (Fan and Roos, 2016; Maidannyk and Roos, 2017; Silalai and Roos, 2011b) also observed that increasing the protein content of dairy systems led to smaller temperature induced changes in the magnitude of the moduli, when measured using DMA. This suggests an increase in the stiffness of these samples, which is likely due to the higher molecular weight of proteins, compared to lactose. In the present study, similarly to the effect of  $a_w$ , this trend was more pronounced in the loss moduli compared to the storage moduli. As the storage modulus is a measure of the elasticity/stiffness of a material (Menard, 2002), it is likely that changes in the stiffness of the sample are more subtle compared to the loss modulus, which indicates changes in viscosity.

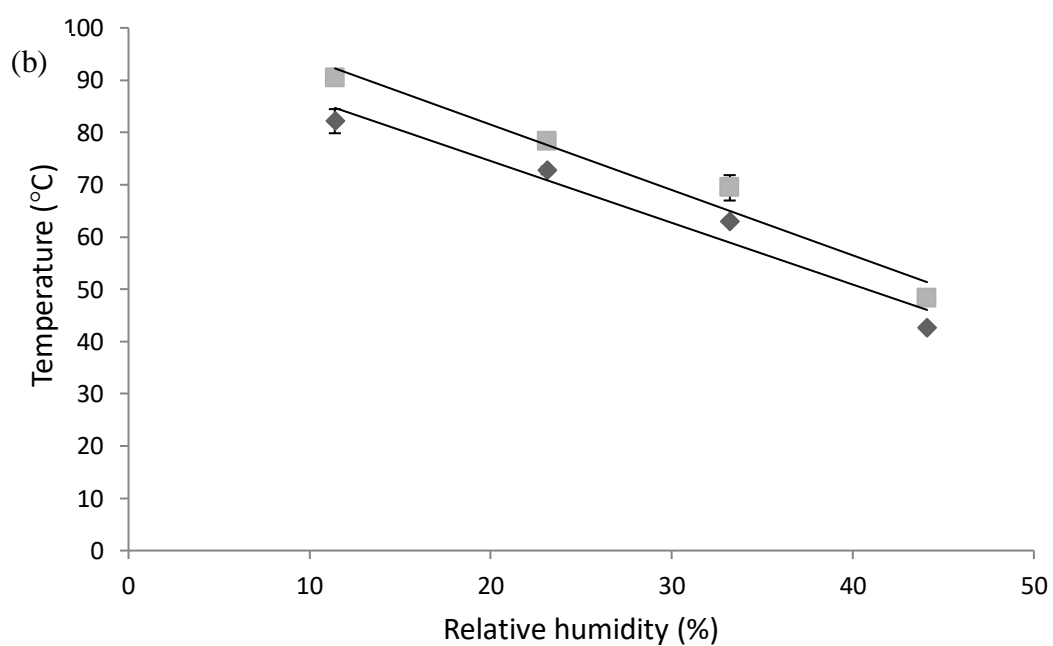
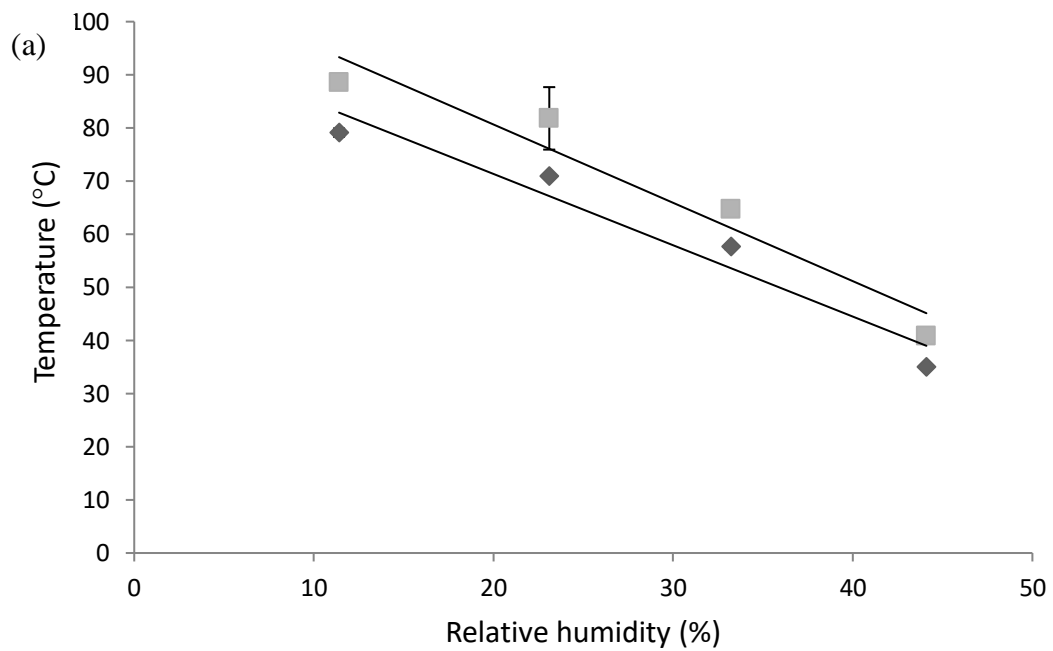




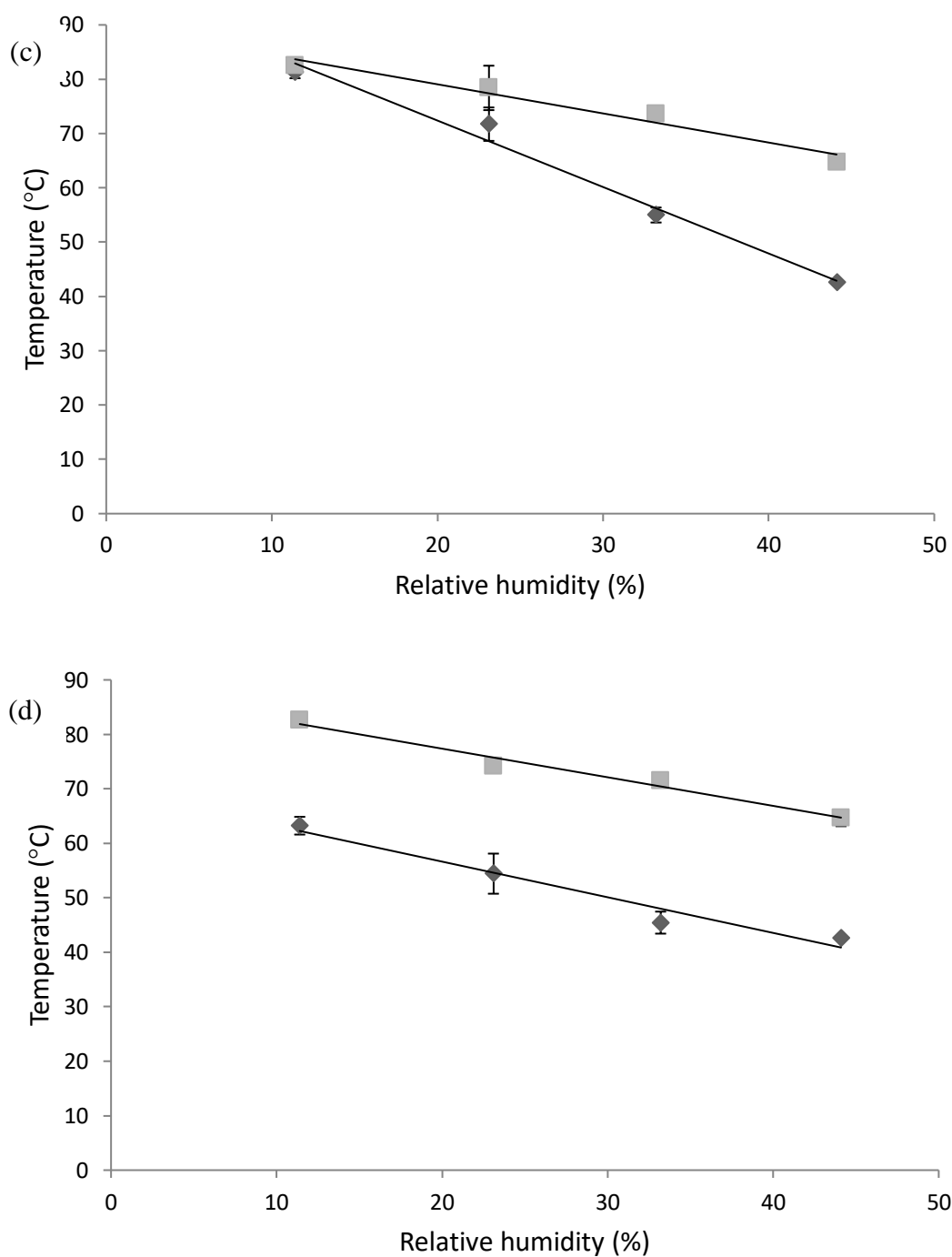
**Figure 3.3** Storage (b) and loss (b) moduli of various whey protein concentrate (WPC) powders; WPC 20 (···), WPC 35 (---), WPC 50 (—○—), and WPC 65 (—), at a water activity ( $a_w$ ) of 0.23.

The DMA profiles or ‘curves’, generated from the  $\alpha$ -relaxation temperatures of the storage and loss moduli, are presented in Fig 3.4. The  $\alpha$ -relaxation temperatures used to generate the curves were (a)  $T_a$  onset – determined from the onset of the decrease in the storage modulus, and (b)  $T_a$  peak – determined from the peak of the loss modulus. All analysis was carried out at the same frequency (10 Hz), as the  $\alpha$ -relaxation temperature has been shown to be frequency dependent (Silalai and Roos, 2011a; Silalai and Roos, 2011b; Kalichevsky et al., 1992). Fig. 3.4 shows that  $T_a$  onset values were consistently lower than  $T_a$  peak values for all powders, as expected (Kalichevsky et al., 1992; Rahman et al., 2007). For the WPC 20 and 35 powders, the  $T_a$  onset and  $T_a$  peak results were in good agreement, with average  $\Delta T$  values across the four water activities of  $8.26 \pm 2.27$  and  $6.42 \pm 1.29^\circ\text{C}$  for WPC 20 and 35, respectively. The  $T_a$  peak data obtained for the WPC 35 also compare well to  $T_a$  peak values (i.e.,  $X^0$  vs  $Y^0$  at  $Z a_w$ ) reported by Silalai and Roos (2011a) for SMP at the same frequency (10 Hz). The average  $\Delta T$  between the  $T_a$  onset and  $T_a$  peak values for the WPC 50 was slightly greater at  $12.2 \pm 9.85^\circ\text{C}$ ; however,  $\Delta T$  at high  $a_w$  was much more

pronounced ( $\sim 20^\circ\text{C}$ ), as can be seen in Fig. 3.4 (c). For WPC 65, the average  $\Delta T$  was the greatest of all the powders at  $21.8 \pm 3.09^\circ\text{C}$ . Studies comparing the  $\alpha$ -relaxation temperatures determined from the storage and loss moduli of DMA method reported a difference of  $\sim 20^\circ\text{C}$  (Kalichevsky et al., 1992) and  $\sim 17^\circ\text{C}$  (Rahman et al., 2007) between the  $T_a$  onset and  $T_a$  peak values for samples of amylopectin and spaghetti, respectively.





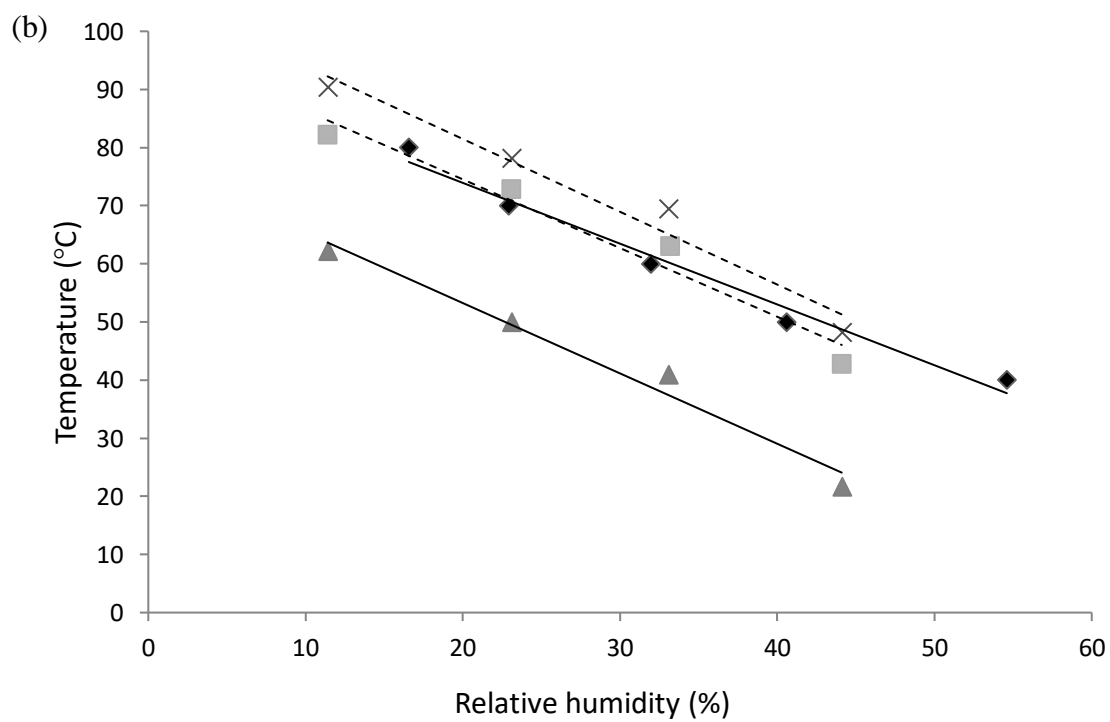
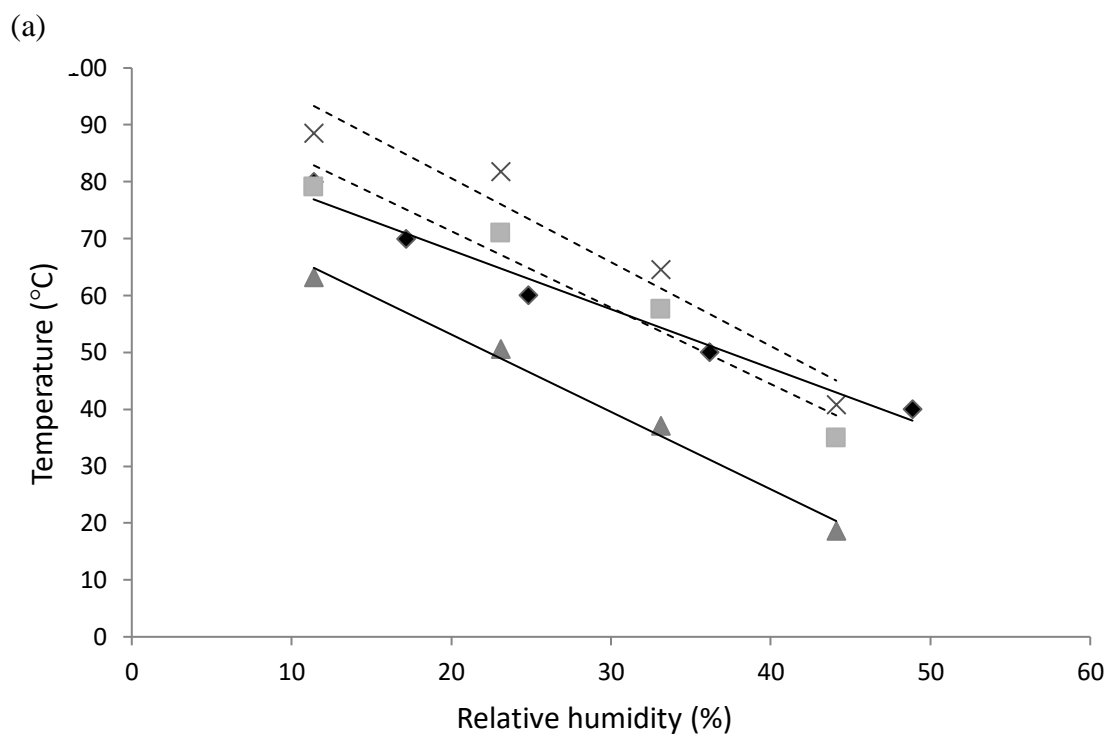


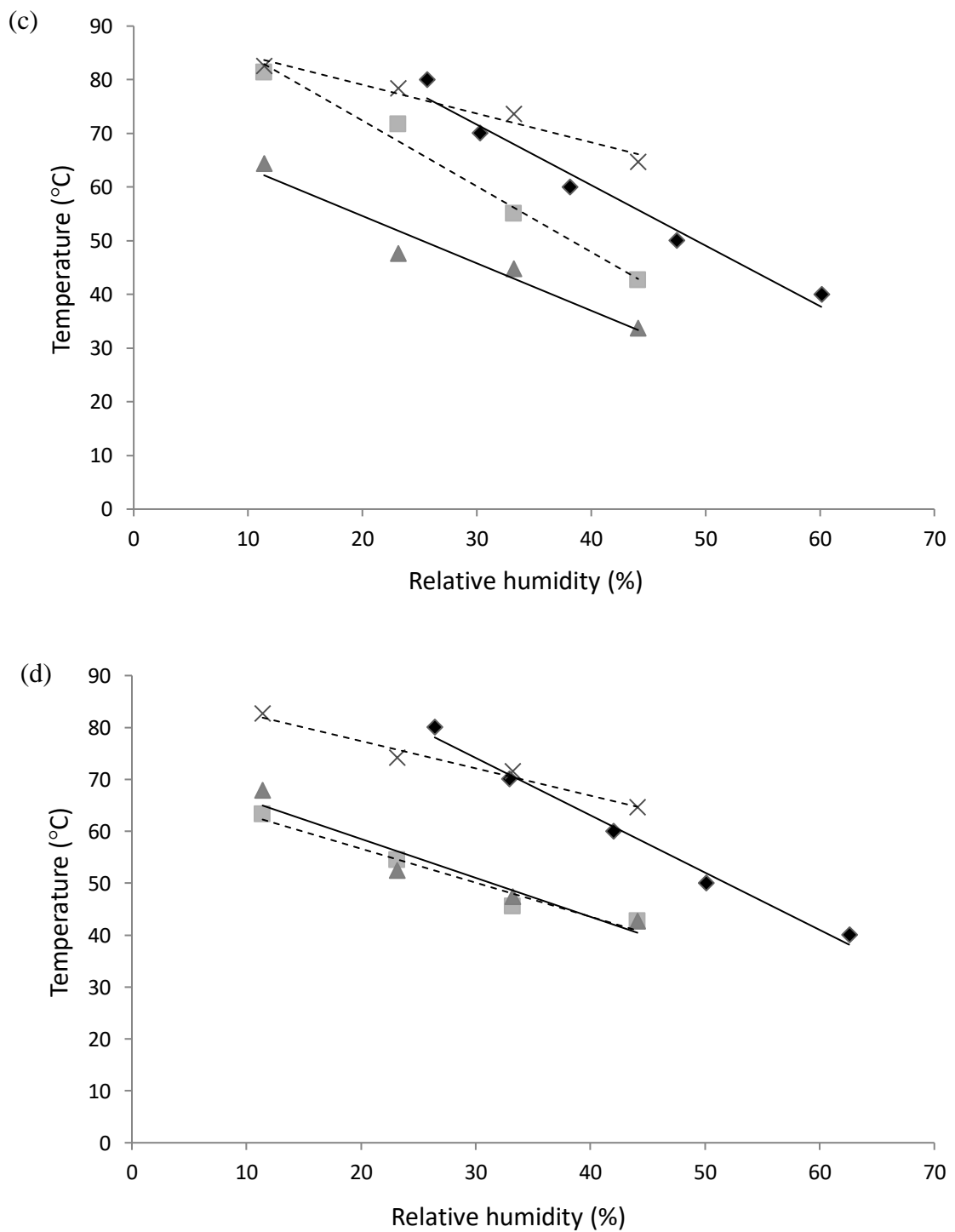
**Figure 3.4** A-relaxation curves determined from the  $T_a$  onset (◆) and the  $T_a$  peak (■) values of the dynamic mechanical analysis (DMA) method for whey protein concentrate (WPC) powders; (a) WPC 20, (b) WPC 35, (c) WPC 50 and (d) WPC 65.

Similar to the stickiness results obtained from the fluidisation method,  $T_a$  onset was found to decrease with increasing  $a_w$  for both moduli (Fig 3.4). Silalai and Roos (2011a) and Maidannyk and Roos (2017) also observed a similar effect of  $a_w$  on  $T_a$  peak for selected dairy powders using DMA. However, unlike the fluidisation results, there was no clear influence of protein/lactose content on the  $T_a$  values of the WPC powders from the results determined from either modulus across the range of water activities. In contrast, other studies (Fan and Roos, 2016; Maidannyk and Roos, 2017; Silalai and Roos, 2011a) have generally found that the presence of protein increased the  $T_a$  peak values of dairy powders.

### 3.3.4 Comparison of $\alpha$ -relaxation, stickiness and glass transition curves

The  $T_a$  values determined from the storage and loss moduli of the DMA method were compared to the stickiness curves (obtained using the fluidisation method) and the glass transition curves (Fig. 3.5). For the lower protein powders (WPC 20 and 35), the  $T_a$  onset results were closer to those generated using the fluidisation method, compared to the  $T_a$  peak results. Furthermore, for these powders, the stickiness curves generated using the fluidisation method and the storage moduli ( $T_a$  onset) of DMA were almost identical (Fig. 3.5 a,b). In contrast, for the higher protein powders (WPC 50 and 65), the  $T_a$  peak results were closer to the fluidisation results. Fig. 3.5 also demonstrates that as the protein content of the powder increased (i.e., lactose content decreased), the  $T_a$  onset curve moved away from the fluidisation curve and closer to the glass transition curve. Furthermore, for the WPC 65 powder, the  $T_a$  onset results of DMA and the glass transition curve were almost indistinguishable. This would suggest that, for powders with higher protein contents, the  $T_a$  onset values obtained from the DMA method may be more representative of the changes occurring during the glass transition, rather than stickiness development.





**Figure 3.5** Stickiness curve for the fluidisation technique (◆) and  $\alpha$ -relaxation profiles for the storage (■) and loss (×) modulus of the dynamic mechanical analysis (DMA) method, and the glass transition curve (▲) for the whey protein concentrate (WPC) powders; (a) WPC 20, (b) WPC 35, (c) WPC 50 and (d) WPC 65.

It has been reported that the mechanical  $\alpha$ -relaxation behaviour, measured using DMA, follows the mobility of the lactose in the milk protein matrix (Silalai and Roos, 2011b). For the current study, considering that protein and lactose exist in separate phases in dairy solid systems, it is likely that the higher protein content of the WPC 65 retarded the movement of the lactose, consequently affecting the structural relaxations. Fan and Roos (2016) found a similar effect of protein on the enthalpy relaxations measured by DSC in lactose/protein mixes. The authors concluded that the presence of protein could affect the enthalpy relaxation results by physically blocking the movement of the lactose. It may therefore be the case that for samples with higher protein contents, the stiffness of the sample is so great that the storage modulus determined using DMA and DSC are measuring the same structural relaxation changes. Furthermore, it should also be noted that the DMA method has been frequently used for determination of glass transition (Bengoechea et al., 2007; Hallberg and Chinachoti, 1992; Kalichevsky et al., 1992; Kararli et al., 1990; Menard, 2002; Rahman et al., 2007; Siebenmorgen et al., 2004); however, the value reported as the  $T_g$  can vary between the onset in the drop of the storage modulus, the peak of the loss modulus, or the onset or peak of the  $\tan \delta$  curve (Menard, 2002).

As previously mentioned, in a study by Silalai and Roos (2011b), the authors compared the results from DMA to the stickiness method modified from the design by Lazar et al. (1956) and concluded that the DMA method was a good indication of stickiness in SMP/maltodextrin mixtures. However, the method developed by Lazar et al. (1956) is a propeller-driven, viscometry technique, and like the DMA method, is performed under relatively static conditions. In contrast, the fluidisation rig used in the current study is a pneumatic technique performed under dynamic conditions. These two types of methods (static vs. dynamic) therefore measure particle interactions under very different conditions. Firstly, static techniques often involve the humidification of powders in desiccators until a desired water activity is reached, which may take days, or even weeks, to complete. Furthermore, the viscometer-based technique requires an additional 20-30 min of pre-conditioning before testing

in order for the sample to equilibrate to the desired temperature (Silalai and Roos, 2010). This may lead to physical changes within certain components of the powder, especially at higher water activities, e.g., water migration and lactose crystallisation. In contrast, the powder in the fluidisation apparatus undergoes a very short conditioning time of several seconds, as the powder comes in contact with the fluidising air. The particle interactions for both methods are also very different. The powder in the viscometer-based technique is in the form of a bed, where particle interactions would be high due to the close contact. However, in the fluidisation method, the particles are suspended in a stream of air and would therefore come into contact less frequently, compared to the viscometer technique. Therefore, it is quite likely that these two types of methods would produce different stickiness results. An example of this can be seen in the study by Murti et al. (2010), in which the authors found a 10-15°C difference in the SPTs of the same powder when measured using a fluid bed and a particle gun. Although these are both pneumatic methods, the air velocities and particle trajectories vary greatly between the two methods. Similarly, in the current study, the SPT/ $T_a$  reported for the WPC 65 powder at an  $a_w$  of approximately 0.33 were very different at 70°C and 45°C, for the fluidisation and DMA ( $T_a$  onset) method, respectively.

### 3.3.5 Comparison of $T-T_g$ results from different measurement techniques

As previously mentioned, the temperature at which sticking occurred in dried amorphous carbohydrate solutions was reported to be approximately 10-15°C above the  $T_g$  (Roos and Karel, 1991b). The  $T-T_g$  therefore represents the temperature increment above the  $T_g$  at which the decrease in surface viscosity has become sufficient in order for sticking to occur. Many studies have demonstrated that the  $T-T_g$  for dairy powders depends on factors such as the powder composition (Hogan et al., 2009) and measurement techniques used (Boonyai et al., 2004). The current study therefore provides an opportunity to compare the various  $T-T_g$  values obtained for the same powders using different measurement techniques (DMA and fluidisation).

**Table 3.3** Difference between temperature ( $T_f$  or  $T_a$ ) and glass transition temperature ( $T_g$ ), determined for whey protein concentrate (WPC) powders with protein contents ranging from ~20 (WPC 20) to ~65% (WPC 65), at the midpoint of the curve and at 15% relative humidity (RH) using the fluidisation or dynamic mechanical analysis (DMA) approach.

Method	Sample	T- $T_g$ at mid pt (°C)	T- $T_g$ at 15% RH (°C)
Fluidisation	WPC 20	18.1	13.2
	WPC 35	23.1	19.9
	WPC 50	22.7	29.5
	WPC 65	18.0	28.4
DMA (storage)	WPC 20	18.3	18.1
	WPC 35	21.5	21.1
	WPC 50	15.1	19.5
	WPC 65	-1.14	-2.35
DMA (loss)	WPC 20	26.6	28.1
	WPC 35	27.9	28.4
	WPC 50	27.1	22.7
	WPC 65	20.6	17.7

The  $T-T_g$  values for the fluidisation and DMA method ( $T_a$  onset and  $T_a$  peak) at selected points along the stickiness/ $\alpha$ -relaxation curves are provided in Table 3.3. The  $T-T_g$  values were determined at two points along the curves for comparison; firstly at the midpoint (x value) of the stickiness/ $\alpha$ -relaxation curves, and secondly at 15% RH. This RH was chosen as it was considered representative of industrial spray drying conditions (Schuck et al., 2008).  $T_f-T_g$  results for the DSC and fluidisation

method, using the midpoint of the stickiness curves, ranged from 18.0-23.2°C across the four water activities, but did not display any obvious trend. In contrast, the  $T_f-T_g$  values determined at 15% RH show a general trend of increasing  $T-T_g$  with increasing protein content, with the exception of the WPC 65 (Table 3.3). In a study by Hogan and O'Callaghan (2010), the authors reported that  $T-T_g$  (determined from the midpoint of the stickiness curves) increased with increasing protein content for selected dairy powders. This is likely due to the preferential sorption of water by the proteins, which delays the rate at which the glass transition occurs, therefore delaying the development of stickiness (Hogan and O'Callaghan, 2010). It should also be noted that in the study by Hogan and O'Callaghan (2010), the authors used the Couchman-Karas equation to predict the  $T_g$  values, which may present a possible reason for the discrepancies in the results between the two studies. Although limited information has been reported on  $T-T_g$  values for WPC powders, the  $T_f-T_g$  values obtained for the WPC 35 sample (23.1 and 19.9°C for the midpoint and 15% RH, respectively), are in good agreement with  $T-T_g$  values reported for SMP of 20.6°C and 23.3°C by O'Donoghue et al. (2019) and Hennigs et al. (2001), respectively.

The  $T_a-T_g$  results from DSC and the storage modulus of DMA ( $T_a$  onset), at both the midpoint and at 15% RH, show an overall decrease in  $T-T_g$  with increasing protein content for WPC powders, with the exception of the WPC 20. However, other studies have reported that the  $T-T_g$  of dairy powders increased with increasing protein content (Hogan and O'Callaghan, 2010; Silalai and Roos, 2010). Nevertheless, for the lower protein powders, the  $T_a-T_g$  values determined from the storage modulus are in good agreement with the  $T_f-T_g$  results found from the fluidisation method in the current study (Table 3). However, for the higher protein powders, the  $T_a-T_g$  values determined from the storage modulus are considerably lower than the  $T_f-T_g$  fluidisation results. Furthermore, as seen in Fig 3.5 (d), the  $\alpha$ -relaxation curve generated from the storage modulus of DMA intersects the glass transition curve for the WPC 65 powder at an  $a_w$  of  $\sim 0.40$ . Therefore, in the current study, negative  $T-T_g$  values were observed for WPC 65 at  $a_w \leq 0.40$  (Table 3), i.e., the reported  $\alpha$ -relaxation temperatures ( $T_a$  onset) occurred below the  $T_g$ . Many studies (Hogan and



O'Callaghan, 2010; Hogan et al., 2009; Ozmen and Langrish, 2002) have shown that the stickiness curve typically tracks the glass transition curve for dairy powders, an observation which is also evident in the current study for the fluidisation and glass transition curves of all four powders (Fig 3.5). However, in the case of the DMA ( $T_a$  onset) curve of the WPC 65 powder, the intersection with the glass transition curve is likely due to the fact that the DMA appears to also be measuring the same structural transition as the DSC.

In the study by Silalai and Roos (2011a), the authors compared stickiness results to the  $\alpha$ -relaxation results from the loss modulus ( $T_a$  peak). In the present study, the  $T_a$ - $T_g$  values calculated from the peaks of the loss moduli range from 20.6-27.9°C and 17.7-28.4°C for the four WPC powders at the midpoint and 15% RH, respectively. Maidannyk and Roos (2017) reported similar  $T_a$ - $T_g$  results of ~20-30°C for a variety of humidified WPI/lactose powders measured using DMA ( $T_a$  peak) and DSC. Similarly, Bengoechea et al. (2007) reported  $T_a$ - $T_g$  values in the range of ~25-40°C when comparing the  $T_a$  peak values from DMA to the  $T_g$  values measured by DSC for samples of casein and soy protein isolate (SPI). In the present study, the  $T_a$ - $T_g$  results obtained from the loss modulus ( $T_a$  peak) were consistently higher than the equivalent results for the storage modulus ( $T_a$  onset) (Table 3.3). While the  $T$ - $T_g$  results for the lower protein powders were higher than those reported for the fluidisation technique, the  $T$ - $T_g$  values found for the loss modulus are more representative of the fluidisation results for the higher protein powders. Overall, these  $T$ - $T_g$  results suggest that for powders with protein contents less than approximately 45% w/w, the results obtained from the  $T_a$  onset values of the DMA method compare well to the  $T$ - $T_g$  obtained from the fluidisation technique, and those reported in the literature. However, for higher protein powders, the  $T$ - $T_g$  results determined from the  $T_a$  peak values of the DMA method may be more representative of the fluidisation results.

### 3.4 Conclusions

DMA was shown to be an interesting complementary technique to other commonly applied methods for measurement of phase transitions ( $T_g$  by DSC) and stickiness behaviour (fluidisation technique) for some dairy powders. The data demonstrated that the comparability to other techniques depends on the composition of the powder and the modulus used ( $T_a$  onset or  $T_a$  peak). The storage modulus results were in good agreement with the stickiness results from the fluidisation technique for lower protein dairy powders (<45% protein w/w), whereas for powders with higher protein contents (~45-65% protein w/w), the results from the loss modulus were found to be more accurate. While DMA may not be a suitable method for stickiness determination, it has potential as a complementary technique that would provide more detailed information on the visco-elastic changes occurring during stickiness development. For example, the results of the current study suggest two different mechanisms of stickiness development; for the lower protein powders stickiness occurs following a reduction in powder stiffness, however, for the higher protein powder, there appears to be a two-stage mechanism involving a reduction in stiffness followed by a significant change in viscosity. It should also be noted that DMA is commonly used for  $T_g$  determination, and in the current study the  $T_a$  onset results were found to be almost identical to the  $T_g$  results obtained using DSC method for the WPC 65. Overall, further research should be carried out in order to gain a deeper understanding of the relationship between  $T_a$  onset,  $T_a$  peak,  $T_g$  and stickiness results.

## **Chapter 4: General discussion and future work**

#### 4.1 General discussion and conclusions

Powder stickiness is a significant challenge faced by dairy processors during spray drying that can lead to considerable economic losses, due to increased down time and reduced powder quality. It is therefore crucial to understand the mechanisms causing stickiness in dairy powders and the factors responsible for its development, in an attempt to minimise its occurrence and severity. In order to do this successfully, good stickiness characterisation techniques that are simple, fast and accurate are essential. However, many of these methods provide binary data (i.e., sticky vs. non-sticky), which while useful, does not help to explain the mechanisms behind stickiness development. The main focus of this work was therefore to gain a deeper understanding of the factors affecting stickiness development and also to explore alternative techniques for stickiness determination. The research presented in this thesis examined the influence of particle size on the stickiness development of three lactose-containing dairy powders. The use of dynamic mechanical analysis (DMA) as a complementary material characterisation technique was also investigated using a selection of whey protein concentrate (WPC) powders, firstly to compare the results to other established stickiness and glass transition determination methods, and secondly to provide more detailed information on the mechanical changes occurring during stickiness development.

In **Chapter 2** of this thesis, stickiness was shown to increase with decreasing particle size in commercial skim milk, whey permeate and demineralised whey powders. One challenge commonly faced by dairy processors during spray drying is blocking of air filtration systems (e.g., cyclones and bag houses) by fine powder particles in the exhaust air. However, with the exception of the preliminary work done by Hogan et al. (2009), there are no studies published directly investigating the effect of particle size on the stickiness behaviour of dairy powders. In the current study, a fluidisation technique was used because it is a dynamic method that more closely represents the conditions within the spray drier compared to other static stickiness characterisation techniques. However, it should also be noted that the stickiness results obtained from the fluid bed are not directly comparable to what is happening in the spray drier

due to differences in the air velocities. Commercial powders were also chosen in order to keep the results as relevant to industry as possible. This study confirmed a commonly-encountered observation in the dairy industry; that smaller particles, or 'fines', exhibit stickier behaviour than larger particles, leading to the blocking of air filtration systems. This was suggested to occur for a variety of reasons, such as; a greater proportion of amorphous lactose in smaller particles compared to larger particles, the increased hygroscopicity of smaller particles and the possible influence of surface fat, in combination with the increased specific surface area (SSA). This study also highlighted the compositional (bulk and surface) and structural differences between the different size fractions of dairy powders containing predominately semi-crystalline or amorphous lactose. For example, bulk composition was shown to be affected by particle size for the two semi-crystalline powders, with protein content reported to increase with decreasing particle size, whereas bulk composition of the agglomerated powder containing predominantly amorphous lactose did not vary with particle size. These differences in bulk composition were found to be the most significant factor contributing to the differences in physicochemical behaviour (e.g., stickiness and hygroscopicity) of these powders.

In **Chapter 3** of this thesis, the results from DMA were compared to methods commonly used to measure phase transitions ( $T_g$  by DSC) and stickiness behaviour (fluidisation technique) of dairy powders and DMA was shown to strongly complement these methods. For dairy powder technology researchers, it is essential that stickiness characterisation techniques are accurate enough to be able to detect small changes in stickiness behaviour between samples. The advantages of DMA are that it is a highly sensitive method, is relatively simple to perform, and as it measures changes in mechanical relaxations; it may also provide a more detailed understanding of the changes in viscoelastic properties that occur during stickiness development. The inspiration for this work came, in part, from a study by Silalai and Roos (2011b), in which the authors compared the results from DMA to a sticky point tester and reported that DMA was a good indicator of stickiness development. However, in the study by Silalai and Roos (2011b), the analysis was conducted on

SMP/maltodextrin powders, which are not very representative of the wide variety of dairy powders produced at large volumes commercially. Therefore, in the current study, a selection of whey protein concentrate powders with a range of protein/lactose contents were chosen. The use of DMA also generated data for a number of mechanical parameters (e.g., storage and loss moduli), from which different values can be determined; the work presented in this thesis compared two data points ( $T_a$  onset - the temperature of the onset of the decrease in the storage modulus, and  $T_a$  peak - the peak temperature of the loss modulus). The DMA results were compared against differential scanning calorimetry (DSC) and a fluidisation method, as they are both considered to be well established and accurate methods for glass transition and stickiness determination, respectively. The results showed that for lower protein powders ( $< \sim 45\%$  protein w/w), the  $T_a$  onset values obtained by DMA agreed well with the stickiness results generated using the fluidisation method. Overall, the results from this study show that while DMA may not be a suitable technique to directly characterise the stickiness behaviour of dairy powders, it may provide more detailed information about the changes occurring in the visco-elastic properties of the powder during stickiness development. DMA may therefore be more useful as a method used for academic study, rather than one that can be implemented directly by industry on-site. However, further research should be carried out on the DMA method as this study also found a link between the glass transition results and the  $T_a$  peak results for the highest protein powder.

In conclusion, this work has contributed to the understanding of a relatively well-described phenomenon, by demonstrating that the stickiness behaviour of a dairy powder should not be determined from the bulk of the powder, as the effect of particle size needs to be considered. This information is particularly useful for dairy processors as they can incorporate these findings into their operational procedures, for example, by changing their drying conditions to alter the particle size distribution of their powders and minimise the amount of fines produced, and therefore reduce issues with stickiness development during drying. However, as the methods used in this research are on a lab scale, the final test of these results will be validation using

an industrial spray drier. In addition, for academic readers, this work has provided an excellent comparison of DMA with another method used to measure phase transitions, DSC, and has also shown a relationship with the stickiness phenomenon. Furthermore, DMA may also provide an opportunity to develop a more mechanistic understanding of stickiness development (i.e., stiffness reduction vs. changes in surface viscosity) in dairy powders; however, further research is required. Depending on the results, this could potentially provide an alternative, very sensitive method to complement stickiness determination which could prove useful to the research community and ultimately benefit manufacturers.

#### **4.2 Recommendations for future work**

Some suitable follow-up studies to the work presented in this thesis include:

- Investigation into the role of surface fat on the stickiness of lactose-containing dairy powders
- Further evaluation of DMA as a complementary stickiness characterisation technique using a wider selection of dairy powders and greater range of parameters (e.g., different frequencies)
- Evaluation of the effect of particle size on the mechanism of stickiness using DMA
- Investigation into the use of DMA for powders considered unsuitable for the traditional stickiness methods outlined in this paper (i.e., powders with high fat or protein contents).

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## Appendix



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## Influence of particle size on the physicochemical properties and stickiness of dairy powders

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### ABSTRACT

The compositional and physicochemical properties of different whey permeate (WPP), demineralised whey (DWP) and skim milk powder (SMP) size fractions were investigated. Bulk composition of WPP and DWP was significantly ( $P < 0.05$ ) influenced by powder particle size; smaller particles had higher protein and lower lactose contents. Microscopic observations showed that WPP and DWP contained both larger lactose crystals and smaller amorphous particles. Bulk composition of SMP did not vary with particle size. Surface composition of the smallest SMP fraction ( $< 75 \mu\text{m}$ ) showed significantly lower protein ( $-9\%$ ) and higher fat ( $+5\%$ ) coverage compared with non-fractionated powders. For all powders, smaller particles were more susceptible to sticking. Hygroscopicity of SMP was not affected by particle size; hygroscopicity of semi-crystalline powders was inversely related to particle size. This study provides insights into differences between size fractions of dairy powders, which can potentially impact the sticking/caking behaviour of fine particles during processing.

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### 1. Introduction

Stickiness and hygroscopicity of powders, especially those with high carbohydrate contents, are major challenges for the dairy industry, particularly during the spray drying process. Sticky powders can become deposited on the walls of the spray drier and block bag-houses and cyclones, decreasing process efficiency, product yield and quality. Stickiness is a surface phenomenon that occurs when the surface of powder particle reaches a critical viscosity (between  $10^6$  and  $10^8 \text{ Pa s}$ ), which allows for the formation of liquid bridges, causing cohesion between colliding particles and/or adhesion to equipment surfaces (Downton, Flores-Luna, & King, 1982). The viscosity of the particle surface is governed by many factors, such as moisture content, the physical state of lactose and temperature (Downton et al., 1982; Hogan, O'Callaghan, & Bloore, 2009). A wide variety of techniques have been developed over the years to determine the conditions at which powders become sticky, with sticking temperature (T) usually reported as a function of relative

humidity (RH) (Boonyai, Howes, & Bhandari, 2006; Hogan et al., 2009; Intipunya, Shrestha, Howes, & Bhandari, 2009; Lazar, Brown, Smith, Wong, & Lindquist, 1956; Murti, Paterson, Pearce, & Bronlund, 2009; Paterson, Bronlund, Zuo, & Chatterjee, 2007; Paterson, Brooks, Bronlund, & Foster, 2005).

Powders containing large amounts of amorphous lactose are particularly susceptible to sticking as amorphous carbohydrates are thermodynamically unstable and undergo a phase transition from a 'glassy' to 'rubbery' state around a critical temperature, known as the glass transition temperature ( $T_g$ ). This transition is also highly dependent on humidity due to the plasticisation effect of water, which lowers  $T_g$  (Haque & Roos, 2004a; Jouppila & Roos, 1994; Ozmen & Langrish, 2002; Roos & Karel, 1991). As the  $T_g$  is exceeded, the molecular mobility of the system will increase and the particle surface viscosity will decrease, leading to the onset of sticking (Foster, Bronlund, & Paterson, 2006). As a consequence of this, stickiness is commonly encountered during spray drying due to high temperature and RH conditions. The temperature difference between the  $T_g$  and sticking point temperature, known as the  $T-T_g$ , has been extensively studied and is often used to describe the sticking behaviour of dairy powders (Hennigs, Kockel, & Langrish, 2001; Hogan et al., 2009; Murti et al., 2009; Ozmen & Langrish,

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2002; Paterson et al., 2005, 2007). It should be noted that the  $T-T_g$  can vary depending on the measurement technique used (Paterson et al., 2005, 2007) and the composition of the powder (Hogan et al., 2009).  $T-T_g$  values reported for SMP vary from 14 to 22 °C, using a thermo-mechanical test (Ozmen & Langrish, 2002), 23.3 °C, using a direct stirrer-type technique (Hennings et al., 2001), 29 °C, using a fluidised bed apparatus (Hogan & O'Callaghan, 2010; Hogan et al., 2009) to 33.6 °C using a particle gun (Murti et al., 2009).

To minimise processing and product quality challenges associated with stickiness, feeds containing large amounts of lactose, such as whey and whey permeates, are often subjected to a pre-crystallisation step before drying to convert the majority of the amorphous lactose (typically 75–80%) into the more stable, crystalline form. However it is not possible to fully crystallise all of the dissolved lactose. Resulting powders are therefore semi-crystalline in nature, as they contain both lactose crystals and a proportion of amorphous lactose (~20–25% of total lactose), in addition to other milk components (Bansal & Bhandari, 2016). These components differ in diffusivity and molecular weight and therefore may not be distributed evenly between size fractions (Meerdink & van't Riet, 1995), leading to differences in stickiness behaviour.

Particle size is thought to play a role in powder stickiness as it has been shown to have a significant effect on the cohesive and adhesive strength of dairy powders (Rennie, Chen, Hargreaves, & Mackereth, 1999). It is commonly observed in industrial settings that the fines exiting the spray dryer with the exhaust air often stick to the surfaces of the air filtration systems (e.g., cyclones and bag houses). However, to date, very little research has been carried out investigating the effect of particle size on the stickiness of dairy powders. As part of a study by Hogan et al. (2009) the authors examined the differences in stickiness behaviour between two SMP samples of different particle sizes ( $D[4,3]$  values of 130 and 61  $\mu\text{m}$ ) but did not find any significant difference between the stickiness of the two size fractions.

The hygroscopicity of a dairy powder describes its final moisture content after exposure to humid air at a constant temperature. Hygroscopicity is closely linked with stickiness, as increased moisture content increases the rate of stickiness development (Murti et al., 2009). Various studies (such as Carpin et al., 2017 and Haque & Roos, 2004b) have investigated the influence of particle size on water absorption by different dairy powders. Haque and Roos (2004b) examined the differences in water uptake of coarse and fine amorphous lactose/protein powders and found that the fine particles absorbed slightly more water than the coarse powder particles at relative vapour pressures ( $RVP$ )  $\leq 33.2\%$ . Similarly, Carpin et al. (2017) found that for crystalline lactose powders, smaller particles showed an increase in water absorption compared with larger particles at  $RHs > 50\%$ . Rogé and Mathlouthi (2000) also showed the same effect of particle size on water uptake for crystalline sucrose.

Many studies (Kim, Chen, & Pearce, 2002, 2005, 2009; Nijdam & Langrish, 2006; Shrestha, Howes, Adhikari, Wood, & Bhandari, 2007) have compared the bulk and surface compositions of various dairy powders and found that the proportions of protein, fat and lactose on the surface of the particle can be significantly different from those in the bulk of the powder. While such observations are useful, information on the relationship between particle size and surface composition is limited. Kim, Chen, and Pearce (2009) sieved a commercial SMP and examined the surface composition of various size fractions but found no significant effect of particle size on surface composition. However, the range of particle sizes examined in the study by Kim et al. (2009) was very small (between 0 and 90  $\mu\text{m}$ ) and therefore not representative of the range of particle sizes typically found in industrially produced powders. To the author's knowledge, there are no published studies

available on the relationship between particle size and surface composition of semi-crystalline dairy powders, such as whey permeates.

The objectives of this study were to characterise the bulk and surface compositions of various size fractions within different dairy powders, and to investigate whether differences exist in the stickiness behaviour and hygroscopicity of these fractions. In particular, the stickiness behaviour of the smaller size fractions, or fines, was of interest, as excessive stickiness in this fraction can be a limiting factor during spray drying.

## 2. Materials and methods

### 2.1. Materials

Demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP) were supplied by local dairy ingredient companies. Saturated salt solutions magnesium chloride ( $\text{MgCl}_2$ ), potassium carbonate ( $\text{K}_2\text{CO}_3$ ) and sodium chloride ( $\text{NaCl}$ ) were purchased from Sigma Aldrich (Co. Wicklow, Ireland).

### 2.2. Powder fractionation

Powders were sieved using a laboratory test sieve shaker (Octagon 200 test sieve shaker, Endecotts Ltd, London, UK) using three different sieve sizes (250, 150 and 75  $\mu\text{m}$ ). The powders were sieved in batches of 300 g at amplitude 7 for 4 min. The powder in each sieve was then weighed to determine the proportion of each size fraction in the original powder. Two batches of the WPP and four batches of the DWP and SMP were sieved in total. All fractions were well mixed, stored in airtight plastic containers and analysed within 2 months.

### 2.3. Particle size distribution

The particle size distributions (PSD) of each powder fraction were measured by laser light scattering using a Mastersizer 3000 (Malvern Instruments Ltd., UK), equipped with an Aero S dry powder dispersion unit. Particle size measurements were recorded as the volume mean diameter ( $D[4,3]$ ).

### 2.4. Powder composition

Total moisture was determined by Karl-Fischer titration using a 784 KFP Titrimo auto-titration system (Metrohm AG, Herisau, Switzerland) as described by GEA (2006). Protein determination was carried out using a LECO Nitrogen Analyser FP-638 (LECO Corporation, Michigan, USA), using a nitrogen-to-protein conversion factor of 6.38. Non-protein nitrogen (NPN) content was measured using the Kjeldahl method, after precipitation of intact proteins using trichloroacetic acid (TCA). In the absence of an accurate method to measure whey:casein ratio in heat treated SMP, the ratio was taken to be 20:80. Lactose content was measured using a lactose assay kit (Megazyme K-LOLAC, Ireland). It should be noted that there was an insufficient amount of powder to test the  $x < 75 \mu\text{m}$  fraction of the DWP for lactose and NPN, so a simple linear regression was carried out to extrapolate the data. For the SMP fractions, lactose content was assumed to be the same as the original powder. Fat content was analysed by Röse-Gottlieb (IDF, 1987). Ash content was determined after overnight incineration in a muffle furnace at 550 °C. Water activity ( $a_w$ ) was determined using a Novasina Labmaster.aw (Novatron Scientific Ltd., UK). Free moisture was determined by oven drying at 86 °C for 6 h.



### 2.5. Lactose crystallinity

Lactose crystallinity (%) was calculated according to the formula described by Schuck and Dolivet (2002):

$$\frac{BWL.19}{L} \times 100$$

where BWL is the bound water content in the lactose ( $\text{g kg}^{-1}$ ) and L is the lactose content ( $\text{g kg}^{-1}$ ).

The BWL was calculated according to the following formula:  $BWL = TW - FW - (0.0152 \cdot CC) - (0.005 \cdot WPC) - (0.0155 \cdot MSSC)$  where TW: total water content ( $\text{g kg}^{-1}$ ), FW: free water content ( $\text{g kg}^{-1}$ ), CC: casein content ( $\text{g kg}^{-1}$ ), WPC: whey protein content ( $\text{g kg}^{-1}$ ) and MSSC: milk salt solution content ( $\text{g kg}^{-1}$ ).

### 2.6. Scanning electron microscopy

Scanning electron microscopy (SEM) was carried out with a field-emission scanning electron microscope (FE-SEM, Zeiss Supra 40 VP Gemini, Darmstadt, Germany) at 2.00 kV. Powder samples were mounted on double-sided carbon tape attached to SEM stubs and lightly coated with chromium (Emitech K575X, Ashford, UK) prior to analysis. Images were taken at 500 $\times$  magnification.

### 2.7. Stickiness

Powder stickiness was determined using a fluidisation technique previously described by Hogan et al. (2009). Stickiness curves were generated by plotting the air (dry bulb) temperature against the RH (calculated from the saturated air temperature and absolute humidity) at which fluidisation ceased. To determine the effect of surface fat on stickiness behaviour, stickiness curves were generated for powders washed in petroleum ether, as described by Kim, Chen, and Pearce (2005).

### 2.8. Powder fluidisation velocity

Minimum air fluidisation velocities were determined using an Anton Paar MCR 302 rheometer (Graz, Austria), equipped with a powder cell attachment. An 80 mL bed of powder was subjected to an increasing air flow (from 0 to 5  $\text{L m}^{-1}$ ) and the minimum air velocity required to fluidise the powder was determined by studying the pressure drop across the powder bed and dividing by the cross sectional area. The air used to fluidise the powders in the powder cell was in compliance with ISO 8573.1, class 1.3.1, with a dew point of  $-20^\circ\text{C}$  and 0.8 kg moisture  $\text{kg}^{-1}$  dry air. All analysis was conducted at room temperature ( $\sim 20^\circ\text{C}$ ). The air velocity ( $\text{m s}^{-1}$ ) passing through each fluid bed in the stickiness apparatus was determined by dividing the total air flow rate (3.5  $\text{L m}^{-1}$ ) by 5 (for each fluid bed) and then dividing by the cross sectional area of one fluid bed.

### 2.9. Differential scanning calorimetry

Powders were analysed without pre-equilibration under controlled atmosphere conditions. The water activity ( $a_w$ ) of the different size fractions varied slightly from 0.34 to 0.36, 0.28 to 0.36 and 0.30 to 0.31 for the DWP, WPP and SMP, respectively. Glass transitions in the three powders were measured using a Q2000 differential scanning calorimeter (DSC; TA Instruments, Crawley, UK) as described by Murphy et al. (2015). Hermetically sealed differential scanning calorimetry (DSC) aluminium pans, containing between 14 and 24 mg of powder, were heated in a nitrogen purged environment using the following method; heating from 0 to  $60^\circ\text{C}$  at  $5^\circ\text{C min}^{-1}$ , cooling from  $60^\circ\text{C}$  to  $-10^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$ , and finally heating at  $5^\circ\text{C}$  to an end

temperature of  $100^\circ\text{C}$ . The  $T_g$  midpoint values were calculated from the second heating cycle and all analyses were completed in at least duplicate.  $T-T_g$  values were calculated as the difference between sticky point temperature (T) and  $T_g$ , and represent a single point between both curves at the  $a_w$  of the powder. For powders washed with petroleum ether  $T_g$  values of the original powder were used.

### 2.10. Hygroscopicity

Powder hygroscopicity was measured according to the method described by Schuck, Jeantet, and Dolivet (2012). Powder samples ( $\sim 2$  g) were placed in desiccators over saturated salts of  $\text{K}_2\text{CO}_3$  at 43% RH. The samples were equilibrated and weighed at regular intervals until a constant weight was observed.

Hygroscopicity was calculated using the following formula:

$$\frac{((w_2 - w_1 - w_0) \times 1000) + (w_1 \times M)}{(w_2 - w_0) \times 10}$$

where  $w_0$  = vial weight (g),  $w_1$  = sample weight (g),  $w_2$  = weight of vial after equilibration (g),  $M$  = % free moisture (% w/w).

### 2.11. Surface analysis of powders

X-ray photoelectron spectroscopy (XPS) measurements were made using a Kratos AXIS Ultra spectrometer (Kratos Analytical Ltd., Manchester, UK). The relative amounts of protein, fat and lactose at the powder surface were determined using a matrix formula created from the elemental compositions of the pure milk components, according to the method described by Faldt, Bergenstahl, and Carlsson (1993). It should be noted that after calculation the WPP tested in this study gave a slight negative surface fat value for all size fractions. Considering that the fat content of the powder was negligible ( $\sim 0.1\%$ , w/w), the equations were adjusted to remove fat; fat content of WPP surfaces were considered to be "not determined".

### 2.12. Statistical analysis

All analyses were carried out in at least duplicate. Statistical analysis was carried out by subjecting data sets to one-way ANOVA with a least significant difference (LSD) test using SPSS for Windows Regression Models (IBM Ireland Ltd., Dublin, Ireland) statistical analysis package. A level of confidence of  $P \leq 0.05$  was used.

## 3. Results

### 3.1. Powder characterisation

#### 3.1.1. Particle size fractions and bulk composition of powders

The proportion of each size fraction in the original powders is shown in Table 1. In all three powders studied, the majority of particles were between 250 and  $75\ \mu\text{m}$ . However, in DWP, the majority of powder particles were between 250 and  $150\ \mu\text{m}$ , compared with WPP and SMP, which mostly contained particles in the range 150 to  $75\ \mu\text{m}$ . Bulk compositional differences were observed between the various size fractions of the original semi-crystalline powders (Table 2). For DWP and WPP, smaller particles contained higher levels of protein and lower levels of lactose compared with larger particles. The same trend was not seen for SMP, which showed no significant variation ( $P > 0.05$ ) in bulk composition between size fractions. Mineral content of DWP and WPP was also significantly higher ( $P \leq 0.05$ ) in smaller size fractions. In a similar study by Carpin et al. (2017), the authors also observed higher protein and mineral contents for smaller particles

**Table 1**

Proportion (% w/w) of each size fraction in original demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP), separated using 250 µm, 150 µm and 75 µm sieves.

Powder	x > 250 µm	250 > x > 150 µm	150 > x > 75 µm	x < 75 µm
DWP (n = 4)	6.52 ± 2.27	69.2 ± 3.74	22.6 ± 5.33	1.65 ± 0.62
WPP (n = 2)	5.36 ± 1.49	21.1 ± 1.79	66.0 ± 3.77	7.60 ± 0.50
SMP (n = 4)	1.42 ± 0.07	38.1 ± 1.12	54.0 ± 1.85	6.53 ± 0.79

of crystalline lactose powder. The average non-protein nitrogen (NPN) content, expressed as a percentage of total nitrogen, was 4.60 ± 0.01, 13.5 ± 2.29 and 35.6 ± 10.6% across all size fractions of SMP, DWP and WPP, respectively.

As expected, DWP and WPP contained a higher amount of lactose (80.2 ± 1.27 and 87.3 ± 0.83%, respectively) compared with SMP (48.5 ± 6.11%). The majority of lactose in DWP and WPP was in the crystalline form ( $\alpha$ -lactose monohydrate). This is a result of the pre-crystallisation step that occurs before spray drying, in which the majority of amorphous lactose present is converted into the more stable, crystalline form. However, for all size fractions studied, DWP contained higher levels of non-crystalline lactose compared with WPP. In WPP, the smaller particles contained much higher levels of amorphous lactose (40.1% of total lactose in x < 75 µm fraction) compared with larger particles (8.60% of total lactose in x > 250 µm fraction). A similar trend was also observed for DWP. Furthermore, representation of SMP crystallinity in terms of  $\alpha$ -lactose monohydrate is not ideal, as unlike during the manufacture of DWP and WPP, a pre-crystallisation step is not performed prior to drying; therefore any lactose crystals present may consist of mixtures of  $\alpha$ - and  $\beta$ -lactose (Jouppila & Roos, 1994). Therefore, caution should be exercised when interpreting SMP crystallinity values (as  $\alpha$ -lactose monohydrate) from Table 2.

### 3.1.2. Surface composition of powders

Surface compositions differed from bulk compositions in the three powders examined (Table 3). Protein and fat contents were higher at the particle surface, while lactose concentrations at the surface were lower than in the bulk. These findings are consistent with other studies in which it was also reported that protein and fat preferentially migrate to the surface of the particle during drying (Nijdam & Langrish, 2006; Shrestha et al., 2007).

Many studies have shown that the surface fat content of dairy powders is significantly higher than the bulk composition (Kim

**Table 3**

Surface composition of original and fractionated demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP), given in percentage protein, fat and lactose coverage.<sup>a</sup>

Powder	Size fraction (µm)	Crude protein (%)	Fat (%)	Lactose (%)
DWP	Original	41.2 ± 0.50 <sup>ac</sup>	28.4 ± 2.72 <sup>a</sup>	30.4 ± 2.16 <sup>a</sup>
	x > 250	42.3 ± 1.00 <sup>bc</sup>	28.3 ± 0.85 <sup>a</sup>	29.4 ± 0.21 <sup>a</sup>
	250 > x > 150	44.0 ± 0.50 <sup>b</sup>	26.7 ± 0.44 <sup>a</sup>	29.3 ± 0.93 <sup>a</sup>
	150 > x > 75	41.6 ± 1.00 <sup>ac</sup>	26.2 ± 3.51 <sup>a</sup>	32.1 ± 2.45 <sup>a</sup>
	x < 75	39.4 ± 1.00 <sup>a</sup>	27.9 ± 0.14 <sup>a</sup>	32.3 ± 0.84 <sup>a</sup>
WPP	Original	54.2 ± 0.00 <sup>a</sup>	n.d.	35.4 ± 0.25 <sup>a</sup>
	x > 250	45.8 ± 3.98 <sup>b</sup>	n.d.	36.5 ± 1.27 <sup>a</sup>
	250 > x > 150	54.6 ± 1.49 <sup>a</sup>	n.d.	36.5 ± 0.51 <sup>a</sup>
	150 > x > 75	51.8 ± 3.49 <sup>ab</sup>	n.d.	35.4 ± 0.76 <sup>a</sup>
	x < 75	49.7 ± 0.50 <sup>ab</sup>	n.d.	35.2 ± 1.01 <sup>a</sup>
SMP	Original	52.4 ± 0.98 <sup>a</sup>	9.56 ± 1.60 <sup>a</sup>	35.9 ± 0.56 <sup>a</sup>
	x > 250	47.6 ± 1.95 <sup>b</sup>	18.5 ± 3.25 <sup>b</sup>	32.5 ± 1.43 <sup>b</sup>
	250 > x > 150	47.6 ± 0.00 <sup>b</sup>	12.2 ± 0.84 <sup>ac</sup>	38.7 ± 0.98 <sup>ac</sup>
	150 > x > 75	47.2 ± 0.49 <sup>b</sup>	11.0 ± 1.76 <sup>ac</sup>	40.2 ± 1.13 <sup>c</sup>
	x < 75	43.8 ± 0.49 <sup>c</sup>	14.8 ± 1.20 <sup>bc</sup>	39.7 ± 1.76 <sup>cd</sup>

<sup>a</sup> For each powder, different superscript letters within the same column represent a significant difference ( $P \leq 0.05$ ); n.d., not determined.

et al., 2009; Nijdam & Langrish, 2006). In the present study, fat coverage of the original SMP was found to be 9.56 ± 1.60%, which is considerably higher than the 1.06 ± 0.07% fat found in the bulk of the powder. Kim et al. (2009) reported a higher surface fat content of 18% for a commercial SMP with a bulk composition of approximately 1% fat, whereas Nijdam and Langrish (2006) reported a surface fat content of approximately 8% for a SMP with 1.10% bulk fat content. Foerster, Gengenbach, Woo, and Selomulya (2016) demonstrated that, for industrially spray-dried powders, it is the atomisation stage (and not the subsequent drying stage), which is the primary determinant of surface composition, and is responsible for overrepresentation of surface fat. It is thought that fat globules are ruptured during atomisation and are spread homogeneously over the droplet surface, creating a thin film of fat. At lower fat concentrations (between 0 and 5%) small changes in bulk fat content of the powder can also cause significant increases in the fat content at the surface (Nijdam & Langrish, 2006). This may have implications on powder stickiness and caking ability, as a higher fat content at the surface can potentially create a more cohesive particle and promote the formation of weak bridges between particles (Nijdam & Langrish, 2006).

**Table 2**

Bulk composition of original and fractionated demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP).<sup>a</sup>

Powder	Size fraction (µm)	True protein (% w/w)	Fat (% w/w)	Total lactose (% w/w)	Ash (% w/w)	Total moisture (% w/w)	Free moisture (% w/w)	Crystalline lactose (%)
DWP	Original	11.4 ± 0.28 <sup>a</sup>	1.11 ± 0.02 <sup>a</sup>	80.2 ± 1.27 <sup>a</sup>	0.70 ± 0.15 <sup>ac</sup>	4.93 ± 0.15 <sup>a</sup>	1.75 ± 0.01 <sup>a</sup>	73.8
	x > 250	8.23 ± 0.04 <sup>b</sup>	0.85 ± 0.00 <sup>b</sup>	88.3 ± 1.05 <sup>b</sup>	0.49 ± 0.15 <sup>ab</sup>	4.93 ± 0.06 <sup>a</sup>	1.34 ± 0.01 <sup>b</sup>	76.2
	250 > x > 150	10.8 ± 0.18 <sup>c</sup>	1.04 ± 0.01 <sup>c</sup>	79.4 ± 0.28 <sup>a</sup>	0.77 ± 0.10 <sup>ac</sup>	4.99 ± 0.22 <sup>a</sup>	1.71 ± 0.05 <sup>a</sup>	76.9
	150 > x > 75	11.8 ± 0.13 <sup>d</sup>	1.16 ± 0.00 <sup>d</sup>	75.4 ± 0.61 <sup>c</sup>	0.79 ± 0.01 <sup>c</sup>	5.10 ± 0.12 <sup>a</sup>	1.86 ± 0.10 <sup>a</sup>	79.9
	x < 75	21.4 ± 0.09 <sup>e</sup>	1.95 ± 0.03 <sup>e</sup>	71.6	1.43 ± 0.11 <sup>d</sup>	5.13 ± 0.08 <sup>a</sup>	3.10 ± 0.26 <sup>c</sup>	50.5
WPP	Original	3.52 ± 0.05 <sup>a</sup>	0.08 ± 0.01 <sup>a</sup>	87.3 ± 0.83 <sup>a</sup>	6.77 ± 0.03 <sup>a</sup>	5.63 ± 0.13 <sup>a</sup>	1.65 ± 0.00 <sup>a</sup>	84.0
	x > 250	0.54 ± 0.02 <sup>b</sup>	0.08 ± 0.01 <sup>a</sup>	99.2 ± 0.94 <sup>b</sup>	1.59 ± 0.02 <sup>b</sup>	5.18 ± 0.28 <sup>b</sup>	0.38 ± 0.00 <sup>b</sup>	91.4
	250 > x > 150	2.89 ± 0.07 <sup>c</sup>	0.11 ± 0.01 <sup>a</sup>	93.1 ± 3.19 <sup>c</sup>	5.89 ± 0.11 <sup>c</sup>	5.57 ± 0.12 <sup>a</sup>	1.46 ± 0.00 <sup>c</sup>	81.6
	150 > x > 75	3.47 ± 0.05 <sup>d</sup>	0.10 ± 0.05 <sup>a</sup>	83.7 ± 1.10 <sup>a</sup>	7.68 ± 0.01 <sup>d</sup>	5.63 ± 0.06 <sup>a</sup>	1.86 ± 0.01 <sup>d</sup>	82.4
	x < 75	6.01 ± 0.01 <sup>e</sup>	0.13 ± 0.01 <sup>a</sup>	70.5 ± 0.06 <sup>d</sup>	12.9 ± 0.12 <sup>e</sup>	5.59 ± 0.10 <sup>a</sup>	3.14 ± 0.00 <sup>e</sup>	59.9
SMP	Original	36.4 ± 0.56 <sup>a</sup>	1.06 ± 0.07 <sup>a</sup>	48.5 ± 6.11	7.31 ± 0.02 <sup>a</sup>	5.52 ± 0.14 <sup>a</sup>	5.05 ± 0.00 <sup>a</sup>	3.28
	x > 250	36.1 ± 0.03 <sup>a</sup>	0.94 ± 0.01 <sup>b</sup>	48.5 ± 6.11	7.19 ± 0.03 <sup>b</sup>	5.47 ± 0.13 <sup>a</sup>	5.04 ± 0.01 <sup>a</sup>	10.9
	250 > x > 150	36.3 ± 0.05 <sup>a</sup>	0.95 ± 0.02 <sup>b</sup>	48.5 ± 6.11	7.24 ± 0.01 <sup>bc</sup>	5.47 ± 0.02 <sup>a</sup>	5.12 ± 0.10 <sup>a</sup>	2.20
	150 > x > 75	36.4 ± 0.05 <sup>a</sup>	0.93 ± 0.02 <sup>b</sup>	48.5 ± 6.11	7.23 ± 0.03 <sup>bd</sup>	5.50 ± 0.04 <sup>a</sup>	5.07 ± 0.01 <sup>b</sup>	8.80
	x < 75	36.5 ± 0.06 <sup>a</sup>	1.00 ± 0.03 <sup>ab</sup>	48.5 ± 6.11	7.25 ± 0.03 <sup>cd</sup>	5.51 ± 0.03 <sup>a</sup>	5.13 ± 0.07 <sup>a</sup>	3.66

<sup>a</sup> For each powder, different superscript letters within the same column represent a significant difference ( $P \leq 0.05$ ). True protein is defined as (Total nitrogen – Non-protein nitrogen) × 6.38; For DWP size fraction x < 75 values for non-protein nitrogen and lactose are extrapolated; for SMP the lactose values were assumed to be constant for all size fractions. Crystalline lactose is  $\alpha$ -lactose monohydrate as a percentage of total lactose.



Particle size can affect surface composition due to differences in droplet drying times, allowing more or less migration of certain milk components to the particle surface. For example, Foerster et al. (2016) reported that protein migration to the particle surface was more prominent in droplets with larger diameters. The authors suggested that this may be due to the surface activity of the protein and differences in diffusivity between the various milk components. In keeping with those observations, Table 3 shows that there was a significant difference ( $P \leq 0.05$ ) in the amount of protein at the surface between the largest and the smallest size fraction of SMP ( $47.6 \pm 1.95\%$  and  $43.8 \pm 0.49\%$ , respectively). However, in a similar study investigating differences in surface composition of various size fractions of SMP, Kim et al. (2009) observed no significant effect of particle size on surface composition. It should be noted that the particle size range used in their study was very small ( $0\text{--}90\text{ }\mu\text{m}$ ) and therefore the differences in size may not have been large enough to show any significant change in surface composition. For DWP and WPP, no clear influence of particle size on surface composition was observed (Table 3). However, disproportionately high levels of crude protein were observed at the surface of WPP powders in comparison with DWP, especially when considering the protein contents of the bulk powders (Table 2). This may indicate a greater diffusivity of nitrogenous compounds in WPP particles during drying.

### 3.1.3. Particle morphology

Scanning electron micrographs of the three original powders and their size fractions are shown in Fig. 1. For DWP and WPP, the semi-crystalline nature of the powders could be clearly seen, as they consisted of a mixture of sharp-edged lactose crystals and less regular/more globular amorphous powder particles. The non-crystalline particles in DWP appeared to be more spherical in shape compared with WPP. This may be due to the higher protein content of DWP, as protein formulation has been shown to influence particle morphology (Maa, Costantino, Nguyen, & Hsu, 1997). The  $x < 75\text{ }\mu\text{m}$  fraction of WPP also appeared to be comprised of smaller particles compared with the equivalent size fraction of DWP and SMP (Fig. 1, Sections 5A–C), which could have implications for the flowability of the powder (Fu et al., 2012). SEM images of SMP showed that the powder consisted mostly of agglomerated particles, and that the degree of agglomeration decreased with decreasing particle size.

The scanning electron micrographs from the two semi-crystalline powders also revealed differences in the types of lactose crystals present. In Fig. 1 (section B1) prism shaped crystals can be seen, whereas the crystals seen in Fig. 1 (section B3) had the characteristic tomahawk shape. Factors such as the level of supersaturation (Herrington, 1934; Parimaladevi & Srinivasan, 2014) and the impurities present (Garnier, Petit, & Coquerel, 2002; Visser & Bennema, 1983) during crystallisation can affect the final lactose crystal shape. For example, Parimaladevi and Srinivasan (2014) showed that higher levels of supersaturation promoted the formation of prism shaped crystals, whereas Visser and Bennema (1983) concluded that tomahawk shaped crystals form as a result of the interference of  $\beta$ -lactose on the crystallisation process.

Another distinguishing feature from the SEM micrographs is the presence of small particulates on the surface of the lactose crystals in both of the semi-crystalline powders. This is likely due to the foam of the mother liquor adhering to the crystal surface during spray drying. Similar particulates were also observed by Kalab, Caric, and Milanovic (1991) in DWP, who describe them as 'lace-like ornamentalations' on the surface of the lactose crystals.

### 3.1.4. Glass transition temperature

Studies have shown that the  $T_g$  of a powder containing amorphous sugar is closely associated with the stickiness of that powder

(Paterson et al., 2005), as the  $T_g$  signifies a decrease in surface viscosity and an increase in molecular mobility (Downton et al., 1982). For the three powders studied,  $T_g$  midpoint decreased in the order WPP < DWP < SMP, with values of  $56.2 \pm 1.26$ ,  $48.5 \pm 0.03$  and  $37.7 \pm 0.08\text{ }^\circ\text{C}$ , respectively.  $T_g$  midpoint of the original powders decreased as the amorphous lactose content of the powders increased; this is in keeping with other studies in which amorphous lactose content has been shown to have the greatest influence on  $T_g$  (Jouppila & Roos, 1994; Shrestha et al., 2007).

## 3.2. Powder stickiness and hygroscopicity

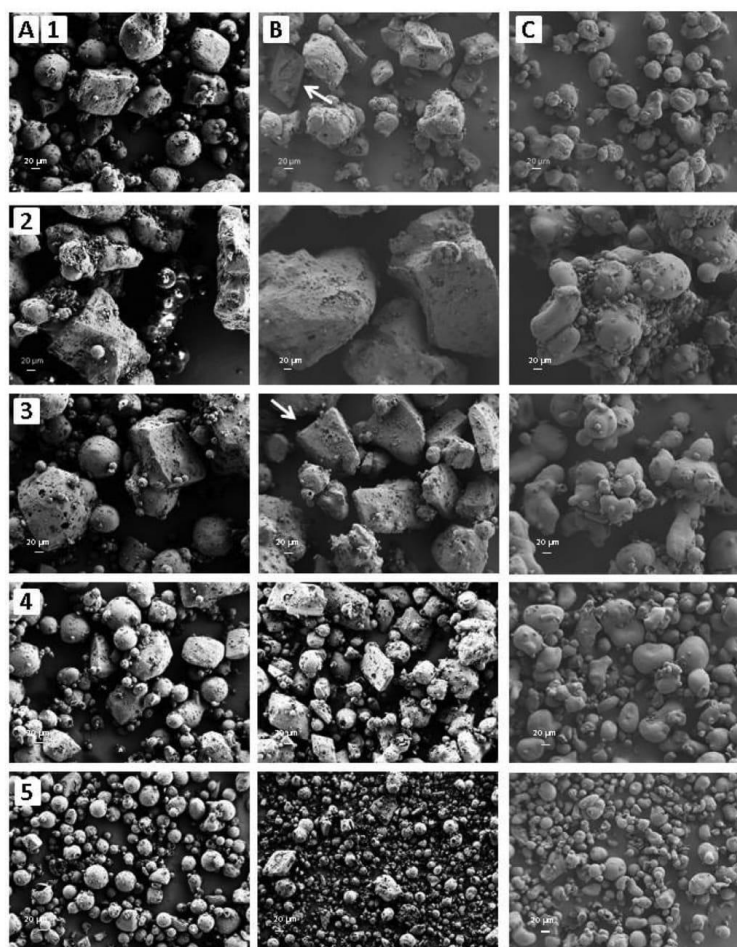
### 3.2.1. Stickiness of non-fractionated powders

Stickiness curves were generated for each powder by plotting the RH against the dry bulb temperature at which the powder became sticky. The areas above and below the curves represent the 'sticky' and 'non-sticky' zones respectively. Fig. 2 shows the stickiness curves for the original DWP, WPP and SMP. For all three powders examined, as the dry bulb temperature increased, the RH at which the powder became sticky decreased. The susceptibility of the powders to sticking increased in the order DWP < WPP < SMP, with SMP exhibiting sticky behaviour at the lowest temperature/RH conditions. Similar results were found by Hogan et al. (2009), who compared the stickiness of various dairy powders, including DWP and SMP.

Of the two semi-crystalline powders examined, WPP was found to be more susceptible to sticking than DWP, despite the fact that WPP had a higher  $T_g$  midpoint and would therefore be expected to have a higher sticking temperature. This may be explained by the higher protein content of DWP ( $11.4 \pm 0.28\%$ ) compared with WPP ( $3.52 \pm 0.05\%$ ); increasing the protein content of lactose-containing powders has been shown to significantly increase the  $T-T_g$ , and therefore protect against sticking (Hogan & O'Callaghan, 2010). This occurs due to the preferential sorption of water by the proteins, which reduces the amount of water available in the system and therefore reduces the rate of plasticisation of amorphous lactose (Hogan & O'Callaghan, 2010; Shrestha et al., 2007). This observation was supported by the  $T-T_g$  values obtained in this study for WPP and DWP (Table 4). In relation to surface composition, WPP was found to have a higher percentage of crude protein at the surface compared with DWP. However, this crude protein value is misleading as it is not possible to differentiate between true protein and NPN using XPS. Based on the bulk composition of the powders, it is probable that a greater proportion of the crude protein at the WPP surface is NPN, which may not have had the same retarding effect as higher molecular weight components on  $T_g$  and stickiness (Roos & Karel, 1991).

### 3.2.2. Influence of particle size on stickiness

Fig. 3 demonstrates the relationship between particle size and stickiness. Smaller particles were more susceptible to sticking in all three powders tested. Stickiness is thought to be influenced by particle size as smaller particles have a higher specific surface area (SSA), which promotes interaction and formation of liquid bridges with one another and/or equipment surfaces. Likewise, inter-particle distance in a given volume will also be affected, resulting in an increase in collision frequency for smaller particles. Another explanation for the increased stickiness observed for the smaller fractions of the semi-crystalline powders could be due to a higher amorphous lactose content, compared with the larger fractions (Hogan & O'Callaghan, 2010; Hogan et al., 2009). However, these results do not agree with the findings by Hogan et al. (2009) who did not observe any effect of particle size on the stickiness of two SMP fractions with D[4,3] values of 130 and  $61\text{ }\mu\text{m}$ . The D[4,3] values of the  $250 > x > 150$  and  $150 > x > 75\text{ }\mu\text{m}$  fractions of SMP



**Fig. 1.** Scanning electron micrographs (500 $\times$  magnification) of (A) demineralised whey powder, (B) whey permeate powder and (C) skim milk powder and their size fractions: (1) original; (2)  $x > 250 \mu\text{m}$ ; (3)  $250 > x > 150 \mu\text{m}$ ; (4)  $150 > x > 75 \mu\text{m}$ ; (5)  $x < 75 \mu\text{m}$ .

examined in this study were 124 and 83.2  $\mu\text{m}$ , respectively. A possible explanation for this disparity may be the use of a vibrating element in the apparatus used by Hogan et al. (2009), which may have served to disrupt inter-particle cohesion in the smaller size fractions. It should also be noted that the stickiness behaviour of the smallest fraction ( $x < 75 \mu\text{m}$ ) of each sample could not be determined due to excessive stickiness under ambient conditions (i.e., air channels developed instantly in the powder and no further fluidisation was observed).

For both of the semi-crystalline powders there was no significant difference ( $P > 0.05$ ) in the amount of lactose present at the surface across the various size fractions (Table 3). However, as previously mentioned, the crystallinity of the lactose in the bulk of the semi-crystalline powders was found to be much higher in larger particles (Table 2). This suggests a higher proportion of amorphous

lactose at the surface of smaller particles, which may have contributed to their sticking behaviour (Murti, 2006). This may also explain the increased stickiness and lower  $T-T_g$  values (Table 4) observed for smaller size fractions of WPP and DWP. For SMP, slightly lower protein and higher lactose contents at the surface of the smaller particles may have accounted for increased stickiness; however, the surface compositional differences observed between fractions were not sufficient to explain the significant differences seen in Fig. 3. For two of the size fractions (i.e., the  $150 > x > 75 \mu\text{m}$  fractions of the DWP and SMP) the  $T-T_g$  had a negative value (Table 4), indicating stickiness occurred prior to glass transition – an observation that contradicts many years of published literature. In light of these findings, further investigation was undertaken to determine if these observations were due to a) fluidisation issues or b) contribution of surface fat to stickiness.



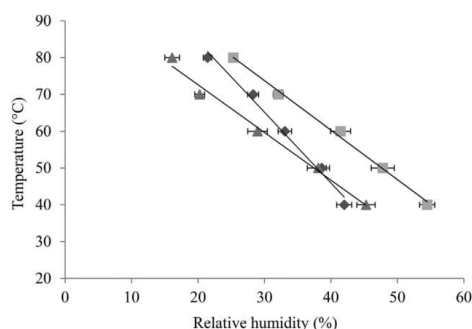


Fig. 2. Stickiness curves of the three original powders examined in the study: (■) demineralised whey powder; (◆) whey permeate powder; (▲) skim milk powder.

To investigate whether the results obtained for the  $x < 75 \mu\text{m}$  fraction were due to poor fluidisation characteristics of the powder, the minimum air velocity required to fluidise each powder fraction was determined by measuring the pressure drop across an 80 mL fluid bed using a powder flow rheometer. For all size fractions tested, the minimum air velocity required to fluidise powders in the rheometer (data not shown) was lower than that passing through the fluid beds ( $0.12 \text{ m s}^{-1}$ ). These findings suggest that the poor fluidisation observed for the  $x < 75 \mu\text{m}$  samples in the stickiness apparatus was likely due to powder stickiness, which inhibited fluidisation due to cohesion between powder particles and/or adhesion of powder particles to the walls of the fluid bed.

Although the amorphous lactose content is considered the predominant cause of stickiness in dairy powders, fat present at the particle surface has also been shown to contribute (Özkan, Walisinghe, & Chen, 2002). To investigate the contribution of surface fat to particle stickiness, a petroleum ether wash was used to remove the surface fat from the  $150 < x < 75 \mu\text{m}$  fractions of all three powders and the  $x < 75 \mu\text{m}$  fraction of SMP. The stickiness behaviour of these fractions was then re-tested and the results are presented in Fig. 4. Both DWP and SMP showed significant improvements in stickiness behaviour for all size fractions after washing (i.e., higher temperature and RH conditions were required for the powders to become sticky). In particular, the  $150 < x < 75 \mu\text{m}$  fraction of DWP showed a very significant

reduction in stickiness, which may be due to the higher amount of surface fat ( $26.2 \pm 3.51\%$ ) removed, compared with the equivalent SMP fraction ( $11.0 \pm 1.76\%$ ). The results for the  $x < 75 \mu\text{m}$  fraction of SMP are also particularly significant, as the stickiness of the previous sample containing surface fat could not be determined using the stickiness rig at all. It should also be noted that the stickiness of WPP could not be re-tested due to extreme caking of the powder after washing.

Particle size and lactose crystallinity of the three powder fractions were re-tested after washing to determine whether any other changes in physicochemical properties of the powders might have affected the stickiness results. The results showed that although there was no change in particle size, the lactose crystallinity of each powder did increase slightly, most likely as a result of exposure to atmospheric conditions during the evaporation of petroleum ether. The  $150 > x > 75 \mu\text{m}$  fraction of DWP had the greatest increase in crystallinity after washing, from 79.9 to 98.0%. The SMP fractions showed smaller increases in crystallinity, from 8.80 to 11.2% for the  $150 > x > 75 \mu\text{m}$  fraction and 3.66 to 4.05% for the  $x < 75 \mu\text{m}$  fraction. The larger increase in lactose crystallinity observed in DWP is likely to have contributed to the considerable improvement in the stickiness behaviour of this powder fraction after washing. Overall, it is difficult to determine the individual influence of the fat removal and the change in lactose crystallinity on the stickiness behaviour of these powder fractions, but considering the magnitude of the change in stickiness behaviour, it is likely a combination of both of these factors. Furthermore, if the surface fat is contributing to stickiness, this, in combination with a higher SSA (and contact between small particles), may help explain the increased stickiness observed in the original  $x < 75 \mu\text{m}$  fractions.

### 3.2.3. Hygroscopicity

Hygroscopicity of the powders is shown in Table 5. Of the three powders examined, SMP was the most hygroscopic ( $7.62 \pm 0.03$  at 43% RH), classifiable as a 'slightly hygroscopic powder' (Table 5). The values obtained for SMP, at 43% RH, are predominantly due to the amorphous lactose content (46.9%) of the powder (Listiophadi, Hourigan, Sleight, & Steele, 2005), in combination with a relatively high protein content ( $36.4 \pm 0.56\%$ ). The two semi-crystalline powders absorbed less moisture than SMP due to their higher crystalline lactose content (Bronlund & Paterson, 2004). Of these, WPP was more hygroscopic ( $3.74 \pm 0.02$  at 43% RH) than DWP ( $2.17 \pm 0.00$  at 43% RH), which may be due to its higher mineral

Table 4

Water activity ( $a_w$ ), glass transition temperature ( $T_g$ ), sticking point temperature (T) and difference between sticking point temperature and glass transition temperature ( $T - T_g$ ) for the original and fractionated demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP), before and after surface fat removal.<sup>a</sup>

Powder	Size fraction ( $\mu\text{m}$ )	Water activity ( $a_w$ )	$T_g$ (midpoint) ( $^{\circ}\text{C}$ )	T ( $^{\circ}\text{C}$ )	$T - T_g$ ( $^{\circ}\text{C}$ )	$T - T_g$ (after washing) ( $^{\circ}\text{C}$ )
DWP	Original	0.34	$48.5 \pm 0.03^a$	68.1	19.6	n.a.
	$x > 250$	0.36	$47.5 \pm 0.13^b$	67.7	20.2	n.a.
	$250 > x > 150$	0.34	$48.8 \pm 0.01^a$	68.5	19.7	n.a.
	$150 > x > 75$	0.35	$49.1 \pm 0.01^a$	42.9	-6.24	104
	$x < 75$	0.34	$48.6 \pm 0.48^a$	n.d.	n.d.	n.e.
WPP	Original	0.27	$56.2 \pm 1.26^a$	70.9	14.7	n.a.
	$x > 250$	0.36	$50.0 \pm 0.83^b$	58.2	8.20	n.a.
	$250 > x > 150$	0.29	$53.7 \pm 0.05^c$	68.7	15.0	n.a.
	$150 > x > 75$	0.28	$54.1 \pm 0.36^c$	62.5	8.35	n.a.
	$x < 75$	0.28	$56.4 \pm 0.30^a$	n.d.	n.d.	n.a.
SMP	Original	0.31	$37.7 \pm 0.08^a$	58.3	20.6	n.a.
	$x > 250$	0.30	$33.4 \pm 0.21^b$	65.1	31.7	n.a.
	$250 > x > 150$	0.31	$39.3 \pm 0.12^c$	60.6	21.3	n.a.
	$150 > x > 75$	0.31	$39.3 \pm 0.93^c$	30.3	-9.00	27.8
	$x < 75$	0.31	$38.2 \pm 0.08^{ac}$	n.d.	n.d.	11.5

<sup>a</sup> For each powder, different superscript letters within the same column represent a significant difference ( $P \leq 0.05$ ); n.d., stickiness could not be determined and therefore  $T - T_g$  could not be calculated; n.e., not enough powder remaining to wash surface; n.a., not analysed.

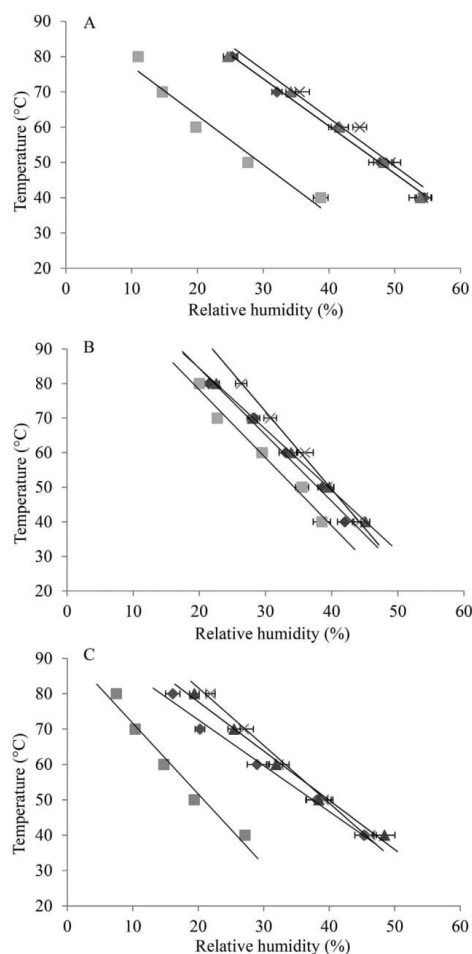


Fig. 3. Stickiness curves showing the original ( $\diamond$ ),  $x > 250 \mu\text{m}$  ( $\times$ ),  $250 > x > 150 \mu\text{m}$  ( $\triangle$ ), and  $150 > x > 75 \mu\text{m}$  ( $\blacksquare$ ) fractions of (A) demineralised whey powder, (B) whey permeate powder and (C) skim milk powder.

content (Ibach & Kind, 2007; Shrestha, Howes, Adhikari, & Bhandari, 2008).

Particle size can also affect the hygroscopicity of a powder as moisture uptake occurs primarily on the particle surface. As such, smaller particle sizes have a relatively larger exchange surface for water absorption to occur, and vice versa. In the current study, powder hygroscopicity increased linearly with decreasing particle size for both DWP and WPP (Table 5). Carpin et al. (2017) observed similar water uptake in smaller size fractions of crystalline lactose powders. This water absorption is likely due to the increased amount of hygroscopic components, such as amorphous lactose, proteins and minerals, present in smaller fractions. However, the same pattern was not observed for the SMP sample, which showed very little variation in hygroscopicity across all size fractions

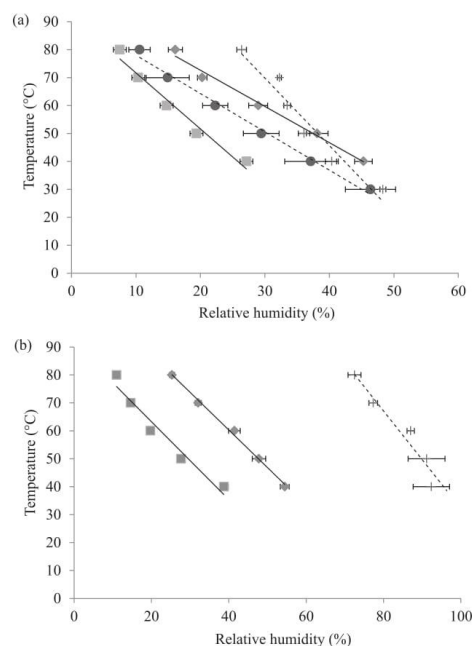


Fig. 4. Stickiness curves showing the ( $\diamond$ ) original, ( $\blacksquare$ )  $150 > x > 75 \mu\text{m}$  (before surface fat removal), ( $+$ )  $150 > x > 75 \mu\text{m}$  (after surface fat removal) and ( $\bullet$ )  $x < 75 \mu\text{m}$  (after surface fat removal) fractions of (A) skim milk powder and (B) demineralised whey powder.

( $7.60 \pm 0.01$  to  $7.78 \pm 0.01$  at 43% RH). These results suggest that the influence of particle size on powder hygroscopicity appears minimal, and that differences in hygroscopicity observed between size

Table 5  
Hygroscopicity of the original and fractionated demineralised whey powder (DWP), whey permeate powder (WPP) and skim milk powder (SMP) at 43% relative humidity (RH).<sup>a</sup>

Powder	Size fraction ( $\mu\text{m}$ )	Hygroscopicity at 43% RH	Classification at 43% RH
DWP	Original	$2.71 \pm 0.00^a$	Non-hygroscopic
	$x > 250$	$2.00 \pm 0.00^b$	Non-hygroscopic
	$250 > x > 150$	$2.61 \pm 0.07^c$	Non-hygroscopic
	$150 > x > 75$	$2.94 \pm 0.02^d$	Non-hygroscopic
	$x < 75$	$5.00 \pm 0.00^e$	Slightly hygroscopic
WPP	Original	$3.74 \pm 0.02^a$	Non-hygroscopic
	$x > 250$	$0.78 \pm 0.01^b$	Non-hygroscopic
	$250 > x > 150$	$3.22 \pm 0.05^c$	Non-hygroscopic
	$150 > x > 75$	$4.23 \pm 0.02^d$	Non-hygroscopic
	$x < 75$	$7.20 \pm 0.03^e$	Slightly hygroscopic
SMP	Original	$7.62 \pm 0.03^a$	Slightly hygroscopic
	$x > 250$	$7.61 \pm 0.02^a$	Slightly hygroscopic
	$250 > x > 150$	$7.78 \pm 0.01^b$	Slightly hygroscopic
	$150 > x > 75$	$7.60 \pm 0.01^a$	Slightly hygroscopic
	$x < 75$	$7.68 \pm 0.03^c$	Slightly hygroscopic

<sup>a</sup> Value ranges for powder hygroscopicity classification at 43% relative humidity (RH) are modified from Schuck et al. (2012): non-hygroscopic,  $\leq 4.5$ ; slightly hygroscopic, 4.6–8.0; hygroscopic, 8.1–11.0; very hygroscopic, 11.1–14.5; extremely hygroscopic,  $\geq 14.5$ . For each powder, different letters within the same column represent a significant difference ( $P \leq 0.05$ ).



fractions of the same powder may be primarily due to differences in composition.

#### 4. Conclusions

The results presented show that significant differences in composition, stickiness behaviour and hygroscopicity exist between the various size fractions of SMP, WPP and DWP. There was a clear distinction observed between powders: DWP and WPP were semi-crystalline powders consisting of mixtures of crystalline lactose and non-crystalline particles, while SMP was composed of largely agglomerated, non-crystalline particles. This distinction was a key determinant in both the fractionation and physicochemical behaviours of resultant powders.

Bulk composition of semi-crystalline powder fractions (DWP and WPP) was greatly affected by particle size; large size fractions were more crystalline compared with smaller fractions, which also had higher protein contents. Smaller size fractions exhibited greater tendency towards stickiness and hygroscopicity, leading to the conclusion that differences in bulk composition were the most significant contributory factor to the differences in physicochemical behaviour. In contrast, bulk composition did not vary across SMP size fractions.

Hygroscopicity of all SMP size fractions was relatively constant, again suggesting that bulk composition was the major determinant for water absorption, rather than particle size. Stickiness behaviour of all three powders, however, was closely related to size, with smaller size fractions exhibiting higher stickiness. It was suggested that this was due to a combination of increased particle surface area and fat coverage.

Overall, this study shows that significant differences exist in stickiness and hygroscopic properties of dairy powders as a function of both composition and particle size. The increased susceptibility of fine particles to stickiness/hygroscopicity is particularly interesting and should be better incorporated into spray drying operational procedures.

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